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(54) Novel transition metal compound, and polymerization catalyst containing it
Übergangsmetallverbindung, und diese enthaltender Polymerisationkatalysator
Nouvelle composé métallique de transition, et catalyseur de polymérisation le contenant

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EP-A- 0 251 771 EP-A- 0 374 695
EP-A- 0 537 686

- ANGEWANDTE CHEMIE. INTERNATIONAL
EDITION, vol.31, no.10, October 1992,
WEINHEIM DE, XP000319626 W.SPALECK 'High
Molecular Weight Polypropylene through
Specifically Designed Zirconocene Catalysts'

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EP 0 629 631 B1

Description

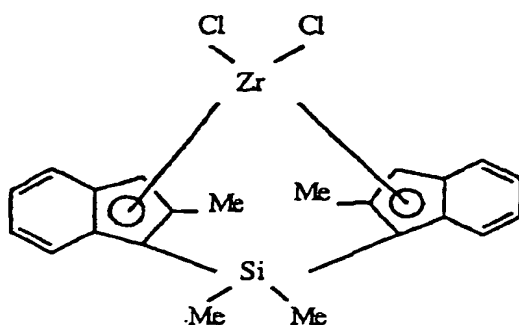
[0001] The present invention relates to a novel transition metal compound, an olefin polymerization catalyst comprising the transition metal compound, and a process for olefin polymerization using the olefin polymerization catalyst.

[0002] A well known homogeneous catalyst is, for example, the so-called Kaminsky catalyst. Use of this Kaminsky catalyst produces a polymer having an extremely high polymerization activity and a narrow molecular weight distribution.

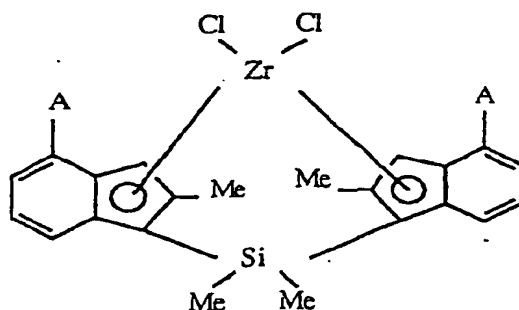
[0003] Of the Kaminsky catalysts, ethylenebis(indenyl)-zirconium dichloride and ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride are known as transition metal compounds for preparing isotactic polyolefins, as described in JP-A-130314/1986. However, polyolefins prepared by the use of these catalysts generally have a low stereoregularity and a low molecular weight. To prepare polyolefins of high stereoregularity and high molecular weight using these catalysts, the polymerization may be conducted at a low temperature, but this has a problem of low polymerization activity.

[0004] It is known that use of hafnium compounds in place of the zirconium compounds makes it possible to prepare a polymer having a high molecular weight, as described in Journal of Molecular Catalysis, 56 (1989), pp. 237-247, but this process also has a problem of low polymerization activity. Dimethylsilyl bisubstituted cyclopentadienyl zirconium dichloride is also known and described in JP-A-301704/1989 and Polymer Preprints, Japan, vol. 39, No. 6, pp. 1,614-1,616 (1990), but this compound is not satisfactory in all of polymerization activity, and stereoregularity and molecular weight of polymers obtained.

[0005] In order to solve these problems, various proposals have been made. For example, JP-A- 268307/1993 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane capable of preparing a high molecular weight polyolefin, but the molecular weight of the resultant polyolefin is still insufficient.



[0006] Further, EP-A-530 648 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane.

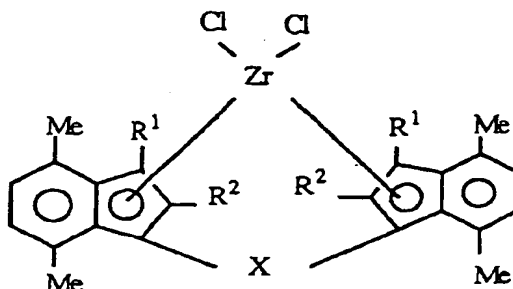


wherein A is a lower alkyl group.

[0007] The molecular weight of the polyolefin obtained by the use of this catalyst is high and industrially satisfactory.

In addition, since the melting point of the polyolefin (e.g., polypropylene) having high stereoregularity becomes high, the catalyst is suitably used for preparing a stereoregular polyolefin having a high melting point. However, it is unsuitable for preparing a stereoregular polyolefin (particularly a copolymer) having a high molecular weight and a low melting point, and the resultant polyolefin or copolymer does not have satisfactory qualities.

[0008] Furthermore, EP-A-537 686 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane.



wherein R¹ and R² are each a methyl group or hydrogen, and X is a Si(CH₃)₂ group or an ethylene group.

[0009] However, a polyolefin obtained by the use of this catalyst has a low molecular weight and cannot be practically used.

[0010] Under the circumstances mentioned above, an olefin polymerization catalyst and a process for olefin polymerization, both having high olefin polymerization activity and being capable of preparing a polyolefin of excellent properties, are desired. The present inventors have found that the above requirements are satisfied by a transition metal compound which has two indenyl groups having a specific substituent group, said two indenyl groups being linked by, for example, a hydrocarbon group or a silicon-containing group.

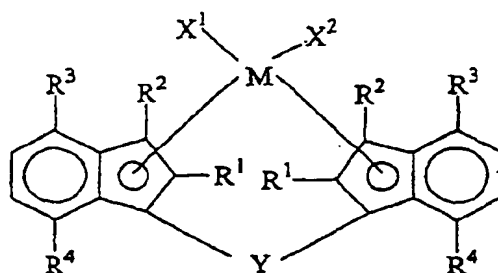
[0011] Propylene polymers have been applied to various uses because of their excellent mechanical properties and optical properties. For example, a propylene homopolymer has excellent rigidity, surface hardness, heat resistance, glossiness and transparency, and hence it is used for various industrial parts, containers, films and nonwoven fabrics. A propylene/ethylene random copolymer containing a small amount of ethylene units has excellent transparency, rigidity, surface hardness, heat resistance and heat-sealing properties, and hence is used for, for example, films or containers. A propylene elastomer has excellent impact absorbing properties, heat resistance and heat-sealing properties, and hence is singly used for films or used as a modifier of a thermoplastic resin.

[0012] However, the conventional propylene polymer does not always have sufficient transparency and impact resistance for some uses, and therefore a propylene polymer having excellent rigidity, heat resistance, surface hardness, glossiness, transparency and impact strength is desired. The conventional propylene/ethylene random copolymer does not always have sufficient transparency, heat-sealing properties, anti-blocking properties, bleed resistance and impact strength for some uses, and therefore a propylene/ethylene random copolymer having excellent transparency, rigidity, surface hardness, heat resistance and heat-sealing properties is desired. The conventional propylene elastomer does not always have sufficient heat-sealing properties, anti-blocking properties and heat resistance when used singly, and does not always have a sufficient effect of improving the impact resistance when used as a modifier. Therefore, a propylene elastomer having excellent impact resistance, heat resistance, transparency, heat-sealing properties, anti-blocking properties and effect of improving impact resistance is desired.

[0013] The present inventors have found that a propylene polymer, propylene copolymer and propylene elastomer which can be prepared by the use of an olefin polymerization catalyst containing the aforesaid specific transition metal compound as a catalyst component have the excellent properties mentioned above.

[0014] The present invention seeks to provide a transition metal compound useful for an olefin polymerization catalyst component having a high olefin polymerization activity.

[0015] The present invention provides a transition metal compound of formula (I):



wherein M is zirconium;

R¹ and R², which may all be identical or different from each other, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms;

R³ is an isopropyl group;

R⁴ is a methyl group;

X¹ and X², which may be identical or different, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms; and

Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylaryl silylene group and an arylsilylene group.

[0016] The present invention also provides an olefin polymerization catalyst comprising:

(A) a transition metal compound of formula (I); and

(B) at least one compound selected from:

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

[0017] The olefin polymerization catalyst may further comprise:

(C) an organoaluminium compound.

[0018] The olefin polymerization catalyst may also further comprise a fine particle carrier, components (A) and (B) being supported on said carrier.

[0019] The olefin polymerisation catalyst alternatively may also further comprise a fine particle carrier and a pre-polymerized olefin polymer produced by pre-polymerization.

[0020] The present invention also provides a process for olefin polymerization comprising polymerizing or copolymerizing an olefin in the presence of an olefin polymerization catalyst as defined above.

[0021] The olefin polymerization catalysts of the invention have high polymerization activity and an olefin polymer obtained by using the catalysts has a narrow molecular weight distribution and a narrow composition distribution. When they are used for polymerizing an α -olefin of 3 or more carbon atoms, a polymer having a lower melting point as compared with a polymer obtained by using a conventional metallocene catalyst, when these polymers have similar molecular weights, can be obtained. Further, in the preparation of a copolymer elastomer containing ethylene or propylene as its major component, a polymer of high molecular weight can be obtained.

[0022] When such catalysts are used, a copolymer having a low melting point can be obtained even though the amount of comonomer units may be small.

[0023] Fig. 1 illustrates the steps of a process for preparing the first and second embodiments of olefin polymerization catalysts of the invention.

[0024] Fig. 2 illustrates the steps of a process for preparing the third and fourth embodiments of olefin polymerization catalysts of the invention.

[0025] Fig. 3 illustrates the steps of a process for preparing the fifth and sixth embodiments of olefin polymerization catalysts of the invention.

[0026] In formula (I), M is zirconium.

[0027] R¹ and R² are each independently a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms.

[0028] Examples of the halogen atoms include fluorine, chlorine, bromine and iodine.

[0029] Examples of the hydrocarbon groups of 1 to 20 carbon atoms include an alkyl group such as methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, icosyl, norbornyl and adamantyl; an alkenyl group such as vinyl, propenyl and cyclohexenyl; an arylalkyl group such as benzyl, phenylethyl and phenylpropyl; and an aryl group such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthracenyl and phenanthryl.

[0030] Of these, R¹ is preferably a hydrocarbon group, particularly a hydrocarbon group of 1 to 3 carbon atoms such as methyl, ethyl and propyl. R² is preferably a hydrogen atom or a hydrocarbon group, particularly a hydrogen atom or a hydrocarbon group of 1 to 3 carbon atoms such as methyl, ethyl and propyl.

[0031] R³ is an isopropyl group and R⁴ is a methyl group.

[0032] X¹ and X² are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms. Examples of those atoms and groups include the halogen atoms and the hydrocarbon groups of 1 to 20 carbon atoms exemplified above with respect to R¹ and R².

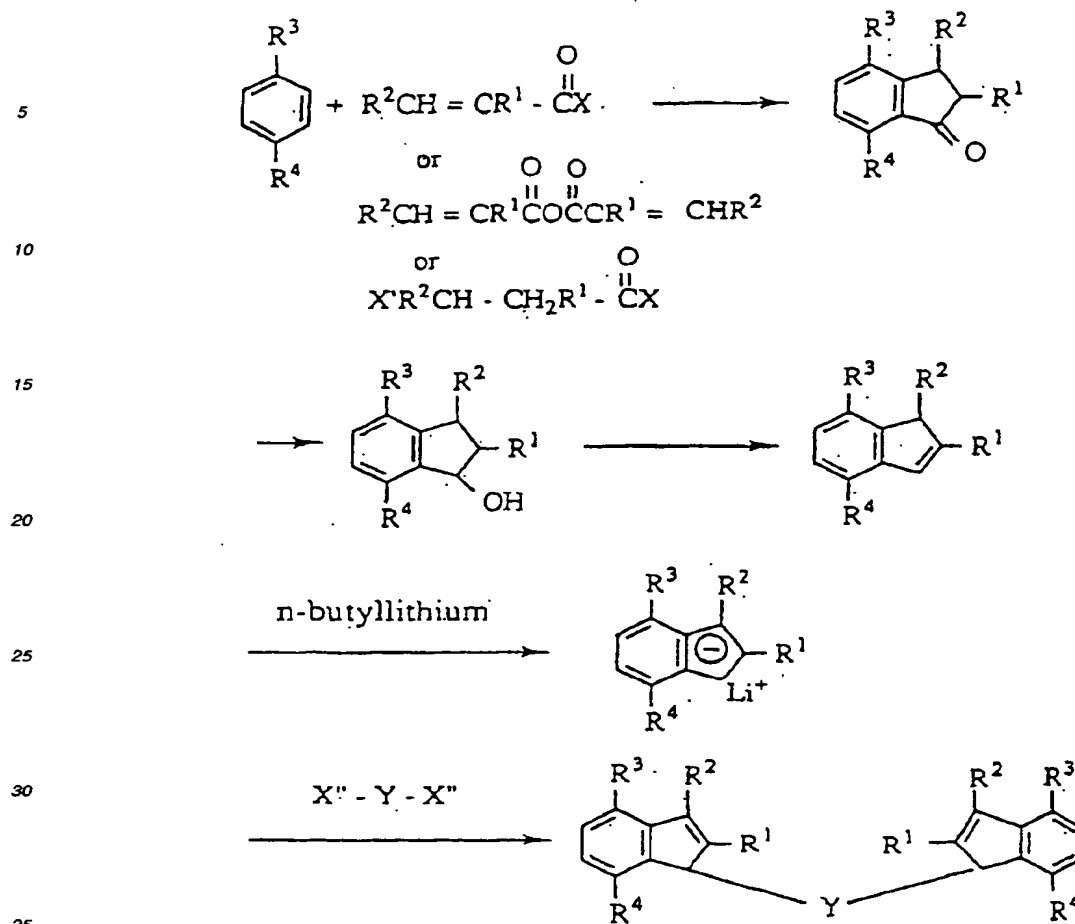
[0033] Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylarylsilylene group and an arylsilylene group.

[0034] Examples of the silicon-containing groups include methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methylphenylsilylene, diphenylsilylene, di(p-tolyl)silylene and di(p-chlorophenyl)silylene.

[0035] Listed below are examples of the transition metal compounds represented by the above formula (I).

rac-Dimethylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diethylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(i-propyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(n-butyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(cyclohexyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Methylphenylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diphenylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-tolyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-chlorophenyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diethylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(i-propyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(n-butyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(cyclohexyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Methylphenylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diphenylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-tolyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-chlorophenyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium dimethyl,
 rac-Dimethylsilyl-bis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium methylchloride,
 rac-Dimethylsilyl-bis{1-(2-methyl-3-methyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-ethyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-phenyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,

[0036] The indene derivative ligand of the transition metal compound of the invention can be synthesized by an organic synthesis method conventionally used through the following reaction route.



(wherein each of X, X' and X'' is a halogen atom.)

[0037] The transition metal compound of the invention can be synthesized from the indene derivative by conventionally known methods, for example, by the method described in JP-A-268307/1993.

[0038] The transition metal compound of the invention can be used as an olefin polymerization catalyst component in combination with an organoaluminium oxy-compound.

[0039] The transition metal compound is usually used as an olefin polymerization catalyst component in the form of a racemic mixture, but the R configuration or the S configuration can be also used.

[0040] The olefin polymerization catalyst containing the above-mentioned transition metal compound as a catalyst component is now described.

[0041] The meaning of the term "polymerization" used herein is not limited to "homopolymerization" but may include "copolymerization". Also, the meaning of the term "polymer" used herein is not limited to "homopolymer" but may include "copolymer".

[0042] The first and second embodiments of olefin polymerization catalysts of the invention are now described.

[0043] The first olefin polymerization catalyst of the invention comprises:

- (A) a transition metal compound of formula (I) (sometimes referred to as "component (A)" hereinafter); and
- (B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

[0044] The second olefin polymerization catalyst of the invention comprises:

- (A) a transition metal compound of formula (I);
(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and
(B-2) a compound which reacts with the transition metal compound to form an ion pair; and

(C) an organoaluminium compound.

[0045] The organoaluminium oxy-compound (B-1) (hereinafter sometimes referred to as "component (B-1)") used for the first and the second olefin polymerization catalysts of the invention may be a conventionally known aluminoxane or may be a benzene-insoluble organoaluminium oxy-compound as described in JP-A-78687/1990.

[0046] The conventionally known aluminoxane can be prepared, for example, by the following processes:

(1) A process comprising allowing an organoaluminium compound such as a trialkylaluminium to react with a suspension of a compound having adsorbed water or a salt containing water of crystallization, for example, the hydrate of magnesium chloride, copper sulfate, aluminium sulfate, nickel sulfate or cerous chloride, in a hydrocarbon solvent.

(2) A process comprising allowing water, ice or water vapor to directly react with an organoaluminium compound such as a trialkylaluminium in a solvent such as benzene, toluene, ethyl ether or tetrahydrofuran.

(3) A process comprising allowing an organotin oxide such as dimethyltin oxide or dibutyltin oxide to react with an organoaluminium compound such as a trialkylaluminium in a solvent such as decane, benzene or toluene.

[0047] The aluminoxane may contain a small amount of an organometallic component. Moreover, the solvent or the unreacted organoaluminium compound may be distilled off from the recovered solution of aluminoxane described above, and the resultant product may be dissolved again in a solvent.

[0048] Examples of the organoaluminium compounds used for preparing the aluminoxane include:

trialkylaluminiums, such as trimethylaluminium, triethylaluminium, tripropylaluminium, triisopropylaluminium, tri-n-butylaluminium, triisobutylaluminium, tri-sec-butylaluminium, tri-tert-butylaluminium, tripentylaluminium, trihexylaluminium, trioctylaluminium and tridecylaluminium;
tricycloalkylaluminiums, such as tricyclohexylaluminium and tricyclooctylaluminium;
dialkylaluminium halides, such as dimethylaluminium chloride, diethylaluminium chloride, diethylaluminium bromide and diisobutylaluminium chloride;
dialkylaluminium hydrides, such as diethylaluminium hydride and diisobutylaluminium hydride;
dialkylaluminium alkoxides, such as dimethylaluminium methoxide and diethylaluminium ethoxide; and
dialkylaluminium aryloxides, such as diethylaluminium phenoxide.

[0049] Of the organoaluminium compounds, trialkylaluminium and tricycloalkylaluminium are particularly preferred.

[0050] Further, there may be also used, as the organoaluminium compound for preparing the aluminoxane, isoprenylaluminium of formula (II):



wherein x, y and z are each a positive number, and $z \geq 2x$.

[0051] The organoaluminium compounds mentioned above may be used singly or in combination.

[0052] Solvents used for preparing the aluminoxane include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions such as gasoline, kerosene and gas oil; and halides of the above-mentioned aromatic, aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. In addition ethers such as ethyl ether and tetrahydrofuran may be also used. Of these solvents, particularly preferred are aromatic hydrocarbons.

[0053] Examples of the compounds which react with the transition metal compound (A) to form an ion pair (hereinafter sometimes referred to as "component (B-2)"), which are used for the first and the second olefin polymerization catalysts, include Lewis acids, ionic compounds, borane compounds and carborane compounds, as described in National Publications of International Patent No. 501950/1989 and No. 502036/1989, JP-A-179005/1992, JP-A-179006/1992, JP-A-207703/1992, JP-A-207704/1992, and US-A-547718.

[0054] The Lewis acid includes an Mg-containing Lewis acid, Al-containing Lewis acid and B-containing Lewis acid. Of these, a B-containing Lewis acid is preferred.

[0055] The Lewis acid containing a boron atom (B-containing Lewis acid) is, for example, a compound of formula:



wherein R^6 , R^7 and R^8 are each independently a phenyl group which may have a substituent such as a fluorine atom, a methyl group or a trifluoromethyl group, or a fluorine atom.

[0056] Examples of the compounds of the above formula include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron. Of these, tris(pentafluorophenyl)boron is particularly preferred.

[0057] The ionic compound used in the invention is a salt comprising a cationic compound and an anionic compound. An anion reacts with the transition metal compound (A) to make the transition metal compound (A) cationic and to form an ion pair so as to stabilize the transition metal cation seed. Examples of such anions include an organoboron compound anion, an organoarsenic compound anion, and an organoaluminium compound anion. Such anions are preferred as they are relatively bulky and stabilize the transition metal cation species. Examples of cations include a metallic cation, organometallic cation, carbonium cation, tripium cation, oxonium cation, sulfonium cation, phosphonium cation and ammonium cation. More specifically, there can be mentioned a triphenylcarbenium cation, tributylammonium cation, N,N-dimethylammonium cation and ferrocenium cation.

[0058] Of these, preferred are ionic compounds containing a boron compound as an anion. More specifically, examples of trialkyl-substituted ammonium salts include triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron, tri(n-butyl)ammoniumtetra(phenyl)boron, trimethylammoniumtetra(p-tolyl)boron, trimethylammoniumtetra(o-tolyl)boron, tributylammoniumtetra(pentafluorophenyl)boron, tripropylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, tri(n-butyl)ammoniumtetra(o-tolyl)boron and tri(n-butyl)ammoniumtetra(4-fluorophenyl)boron.

[0059] Examples of N,N-dialkylanilinium salts include N,N-dimethylaniliniumtetra(phenyl)boron, N,N-diethylaniliniumtetra(phenyl)boron and N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

[0060] Examples of dialkylammonium salts include di(n-propyl)ammoniumtetra(pentafluorophenyl)boron and dicyclohexylammoniumtetra(phenyl)boron.

[0061] Examples of triarylphosphonium salts include triphenylphosphoniumtetra(phenyl)boron, tri(methylphenyl)phosphoniumtetra(phenyl)boron and tri(dimethylphenyl)phosphoniumtetra(phenyl)boron.

[0062] Also employable as the ionic compound containing a boron atom are triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate and ferroceniumtetrakis(pentafluorophenyl)borate.

[0063] Further, the following compounds can be also employed. (In the ionic compounds enumerated below, the counter ion is tri(n-butyl)ammonium, but the counter ion is in no way limited thereto.)

[0064] That is, there can be mentioned salts of anions, for example, bis{tri(n-butyl)ammonium}nonaborate, bis{tri(n-butyl)ammonium}decaborate, bis{tri(n-butyl)ammonium}undecaborate, bis{tri(n-butyl)ammonium}dodecaborate, bis{tri(n-butyl)ammonium}decachlorodecaborate, bis{tri(n-butyl)ammonium}dodecachlorodecaborate, tri(n-butyl)ammonium-1-carbadecaborate, tri(n-butyl)ammonium-1-carbaundecaborate, tri(n-butyl)ammonium-1-carbadecaborate, tri(n-butyl)ammonium-1-trimethylsilyl-1-carbadecaborate and tri(n-butyl)ammoniumbromo-1-carbadecaborate.

[0065] Moreover, borane compounds and carborane compounds can be also employed. These compounds are employed as the Lewis acid or the ionic compounds.

[0066] Examples of the borane compounds and the carborane compounds include:

borane and carborane complex compounds and salts of carborane anion, for example, decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane, dodecahydride-11-methyl-2,7-dicarbaundecaborane, tri(n-butyl)ammonium-6-carbadecaborate(14), tri(n-butyl)ammonium-6-carbadecaborate (12), tri(n-butyl)ammonium-7-carbaundecaborate(13), tri(n-butyl)ammonium-7,8-dicarbaundecaborate(12), tri(n-butyl)ammonium-2,9-dicarbaundecaborate(12), tri(n-butyl)ammoniumdodecahydride-8-methyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-9-trimethylsilyl-7,8-dicarbaundecaborate and tri(n-butyl)ammoniumundecahydride-4,6-dibromo-7-carbaundecaborate; and carborane and salts of carborane, for example, 4-carbanonaborane(14), 1,3-dicarbanonaborane(13), 6,9-dicarbaundecaborane(14), dodecahydride-1-phenyl-1,3-dicarbanonaborane, dodecahydride-1-methyl-1,3-dicarbanonaborane and undecahydride-1,3-dimethyl-1,3-dicarbanonaborane.

[0067] Furthermore, the following compounds can be also employed. (In the ionic compounds enumerated below, the counter ion is tri(n-butyl)ammonium, but the counter ion is in no way limited thereto.)

[0068] That is, there can be mentioned salts of metallic carborane and metallic borane anion, for example, tri(n-butyl)ammoniumbis(nonahydride-1,3-dicarbononaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)nickelate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cuprate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)aurate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)chromate(III), tri(n-butyl)ammoniumbis(tribromooctahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(dodecahydride-dicarbododecaborate)-cobaltate(III), bis(tri(n-butyl)ammonium)bis(dodecahydride-dodecaborate)-nickelate(III), tris(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)chromate(III), bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)manganate(IV), bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)cobaltate(III) and bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)nickelate(IV).

[0069] The compounds (B-2) which react with the transition metal compound (A) to form an ion pair can be used in combination of two or more kinds.

[0070] The organoaluminium compound (C) (hereinafter sometimes referred to as "component (C)") used for the second olefin polymerization catalyst of the invention is, for example, an organoaluminum compound of formula (III):



wherein R^9 is a hydrocarbon group of 1 to 12 carbon atoms, X is a halogen atom or a hydrogen atom, and n is 1 to 3.

[0071] In formula (III), R^9 is, for example, an alkyl group, a cycloalkyl group or an aryl group. Particular examples include methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl.

[0072] Examples of such organoaluminium compounds (C) include:

trialkylaluminiums, such as trimethylaluminium, triethylaluminium, triisopropylaluminium, triisobutylaluminium, trioctylaluminium and tri(2-ethylhexyl) aluminium;
alkenylaluminiums, such as isoprenylaluminium,
dialkylaluminium halides, such as dimethylaluminium chloride, diethylaluminium chloride, diisopropylaluminium chloride, diisobutylaluminium chloride and dimethylaluminium bromide;
alkylaluminium sesquihalides, such as methylaluminium sesquichloride, ethylaluminium sesquichloride, isopropylaluminium sesquichloride, butylaluminium sesquichloride and ethylaluminium sesquibromide;
alkylaluminium dihalides, such as methylaluminium dichloride, ethylaluminium dichloride, isopropylaluminium dichloride and ethylaluminium dibromide; and
alkylaluminium hydrides, such as diethylaluminium hydride and diisobutylaluminium hydride.

[0073] Also employable as the organoaluminium compound (C) is a compound of formula (IV):



wherein R^9 is the same hydrocarbon as in the above formula (III); L is an $-OR^{10}$ group, $-OSiR^{11}_3$ group, $-OAlR^{12}_2$ group, $-NR^{13}_2$ group, $-SiR^{14}_3$ group or $-N(R^{15})AlR^{16}_2$ group; n is 1 to 2; R^{10} , R^{11} , R^{12} and R^{16} are each, for example, methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl; R^{13} is, for example, hydrogen, methyl, ethyl, isopropyl, phenyl or trimethylsilyl; and R^{14} and R^{15} are each, for example, methyl or ethyl.

[0074] Examples of such organoaluminium compounds (C) include:

- (1) compounds of formula $R^9_n Al(OR^{10})_{3-n}$, for example, dimethylaluminium methoxide, diethylaluminium ethoxide and diisobutylaluminium methoxide;
- (2) compounds of formula $R^9_n Al(OSiR^{11}_3)_{3-n}$, for example, $Et_2Al(OSiMe_3)$, $(iso-Bu)_2Al(OSiMe_3)$ and $(iso-Bu)_2Al(OSiEt_3)$;
- (3) compounds of formula $R^9_n Al(OAlR^{12}_2)_{3-n}$, for example, $Et_2AlOAlEt_2$ and $(iso-Bu)_2AlOAl(iso-Bu)_2$;
- (4) compounds of formula $R^9_n Al(NR^{13}_2)_{3-n}$, for example, Me_2AlNEt_2 , $Et_2AlNHMe$, $Me_2AlNHet$, $Et_2AlN(SiMe_3)_2$ and $(iso-Bu)_2AlN(SiMe_3)_2$;
- (5) compounds of formula $R^9_n Al(SiR^{14}_3)_{3-n}$, for example, $(iso-Bu)_2AlSiMe_3$; and

(6) compounds of formula $R^9_nAl(N(R^{15})AlR^{16}_2)_{3-n}$, for example, $Et_2AlN(Me)AlEt_2$ and $(iso-Bu)_2AlN(Et)Al(iso-Bu)_2$.

[0075] Of the organoaluminium compounds of formulae (III) and (IV), the compounds of formulae R^9_3Al , $R^9_nAl(OR^{10})_{3-n}$ and $R^9_nAl(OAIR^{12}_2)_{3-n}$ are preferred, and the compounds having these formulae wherein R is an isoalkyl group and n is 2 are particularly preferred.

[0076] In the present invention, water may be used as a catalyst component in addition to component (A), component (B-1), component (B-2) and component (C). As the water employable in the invention, there can be mentioned water dissolved in a polymerization solvent described later, and adsorbed water or water of crystallization contained in a compound or a salt used for preparing component (B-1).

[0077] The first olefin polymerization catalyst of the invention can be prepared by mixing component (A) and component (B-1) (or component (B-2)), and if desired water (as a catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent).

[0078] There is no specific limitation on the order of mixing those components, but it is preferred that component (B-1) (or component (B-2)) is mixed with water, followed by mixing with component (A).

[0079] The second olefin polymerization catalyst of the invention can be prepared by mixing component (A), component (B-1) (or component (B-2)) and component (C), and if desired water (as a catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent).

[0080] There is no specific limitation on the order of mixing those components. However, when component (B-1) is used, it is preferred that component (B-1) is mixed with component (C), followed by mixing with component (A). When component (B-2) is used, it is preferred that component (C) is mixed with component (A), followed by mixing with component (B-2).

[0081] In the mixing of each component, the atomic ratio (Al:transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 10,000:1, preferably 20:1 to 5,000:1; and the concentration of component (A) is 10^{-8} to 10^{-1} mol/liter-medium, preferably 10^{-7} to 5×10^{-2} mol/liter-medium.

[0082] When component (B-2) is used, the molar ratio (component (A):component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1, and the concentration of component (A) is 10^{-8} to 10^{-1} mol/liter-medium, preferably 10^{-7} to 5×10^{-2} mol/liter-medium.

[0083] In the preparation of the second olefin polymerization catalyst of the invention, the atomic ratio ($Al_C:Al_{B-1}$) of the aluminum atoms (Al_C) in component (C) to the aluminum atoms (Al_{B-1}) in component (B-1) is usually 0.02:1 to 20:1, preferably 0.2:1 to 10:1.

[0084] When water is used as a catalyst component, the molar ratio ($Al_{B-1}:H_2O$) of the aluminum atoms (Al_{B-1}) in component (B-1) to water (H_2O) is 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0085] The above-mentioned components may each be mixed in a polymerizer, or a mixture of those components beforehand prepared may be fed to a polymerizer.

[0086] If the components are beforehand mixed, the mixing temperature is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0087] Examples of the media (solvents) used for preparing the olefin polymerization catalyst according to the invention includes:

aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosene;

alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane;

aromatic hydrocarbons, such as benzene, toluene and xylene;

halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons.

[0088] Next, the third and fourth embodiments of olefin polymerization catalysts of the invention are described.

[0089] The third olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I); and

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair;

said transition metal compound (A) and said at least one compound (B) being supported on the fine particle carrier.

[0090] The fourth olefin polymerization catalyst of the invention comprises:

a solid catalyst component comprising:

a fine particle carrier,

(A) a transition metal compound of formula (I), and
(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair,

said transition metal compound (A) and said at least one compound (B) being supported on the fine particle carrier; and
(C) an organoaluminium compound.

[0091] The transition metal compound (A) used for the third and fourth olefin polymerization catalysts of the invention is the same as that for the aforesaid first and second olefin polymerization catalysts, and is represented by the above formula (I).

[0092] Examples of the organoaluminium oxy-compounds (B-1) used for the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0093] Examples of the compounds (B-2) which react with the transition metal compound (A) to form an ion pair and used for the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0094] Examples of the organoaluminium compounds (C) used for the fourth olefin polymerization catalyst of the invention are the same as those used for the second olefin polymerization catalyst.

[0095] The fine particle carrier used for the third and fourth olefin polymerization catalysts of the invention is an inorganic or organic compound, and is a particulate or granular solid having a particle diameter of 10 to 300 μm , preferably 20 to 200 μm .

[0096] The inorganic carrier is preferably a porous oxide, and examples include SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , and mixtures thereof such as $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr}_2\text{O}_3$ and $\text{SiO}_2\text{-TiO}_2\text{-MgO}$. Of these, preferred is a carrier containing SiO_2 and/or Al_2O_3 as its major component.

[0097] The above-mentioned inorganic oxides may contain carbonates, sulfates, nitrates and oxides, such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O and Li_2O , in a small amount.

[0098] The properties of the fine particle carrier vary depending on the kind and process for the preparation thereof, but a preferred carrier has a specific surface area of 50 to 1,000 m^2/g , preferably 100 to 700 m^2/g , and a pore volume of 0.3 to 2.5 cm^3/g . The fine particle carrier is used after being calcined, if necessary, at 100 to 1,000 $^\circ\text{C}$, preferably 150 to 700 $^\circ\text{C}$.

[0099] Also employable as the fine particle carrier in the invention is a granular or particulate solid of an organic compound having a particle diameter of 10 to 300 μm .

Examples of the organic compounds include (co)polymers prepared mainly from α -olefins of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, and (co)polymers prepared mainly from vinylcyclohexane or styrene.

[0100] The fine particle carrier may contain surface hydroxyl groups or water. In this case, the surface hydroxyl groups are contained in an amount of not less than 1.0 % by weight, preferably 1.5 to 4.0 % by weight, more preferably 2.0 to 3.5 % by weight; and water is contained in an amount of not less than 1.0 % by weight, preferably 1.2 to 20 % by weight, more preferably 1.4 to 15 % by weight. The water contained in the fine particle carrier means water which is adsorbed on the surface of the fine particle carrier.

[0101] The amount (% by weight) of the adsorbed water and the amount (% by weight) of the surface hydroxyl group in the fine particle carrier can be determined in the following manner.

Amount of adsorbed water

[0102] The weight reduction of the fine particle carrier after drying at 200 $^\circ\text{C}$ under ordinary pressure for 4 hours in

a stream of nitrogen is measured, and the percentage of the weight after the drying to the weight before the drying is calculated.

Amount of surface hydroxyl groups

[0103] The weight of the fine particle carrier after drying at 200 °C under ordinary pressure for 4 hours in a stream of nitrogen is taken as X (g). The carrier is calcined at 1,000 °C for 20 hours to obtain a calcined product containing no surface hydroxyl groups. The weight of the calcined product thus obtained is taken as Y (g). The amount (% by weight) of the surface hydroxyl groups is calculated from the following formula.

$$\text{Amount (wt.\%) of surface hydroxyl groups} = \{(X-Y)/X\} \times 100$$

[0104] If a fine particle carrier having a specific amount of adsorbed water or a specific amount of surface hydroxyl groups as described above is used, an olefin polymerization catalyst capable of preparing an olefin polymer having excellent particle properties and having a high polymerization activity can be obtained.

[0105] Further, in the third and the fourth olefin polymerization catalysts of the invention, water as described in the first and second olefin polymerization catalysts may be used as a catalyst component.

[0106] The third olefin polymerization catalyst of the invention (i.e., solid catalyst component) can be prepared by mixing the fine particle carrier, component (A) and component (B-1) (or component (B-2)), and, if desired, water (catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent). In the mixing of those components, component (C) can be further added.

[0107] There is no specific limitation on the order of mixing those components.

[0108] However, preferred processes are:

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)), and then with component (A), followed by mixing with water if desired;

a process in which a mixture of component (B-1) (or component (B-2)) and component (A) is mixed and contacted with the fine particle carrier, followed by mixing with water if desired; and

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)) and water, followed by mixing with component (A).

[0109] In the mixing of each components, component (A) is usually used in an amount of 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, per 1 g of the fine particle carrier; and the concentration of component (A) is generally 5×10^{-6} to 2×10^{-2} mol/liter-medium, preferably 2×10^{-5} to 10^{-2} mol/liter-medium. The atomic ratio (Al: transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 3,000:1; preferably 20:1 to 2,000:1. When component (B-2) is used, the molar ratio (component (A): component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1.

[0110] When water is used as a catalyst component, the molar ratio (Al_{B-1}:H₂O) of the aluminium atoms (Al_{B-1}) in component (B-1) to water (H₂O) is range of 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0111] The temperature for mixing the components is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0112] The fourth olefin polymerization catalyst of the invention is formed from the above-mentioned third olefin polymerization catalyst (solid catalyst component) and the organoaluminium compound (C). Component (C) is used in an amount of not more than 500 mol, preferably 5 to 200 mol, per 1 g of the transition metal atoms in component (A) contained in the solid catalyst component.

[0113] The third and the fourth olefin polymerization catalysts of the invention may contain other components useful for olefin polymerization.

[0114] Examples of the inert hydrocarbon media (solvents) used for preparing the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0115] Next, the fifth and the sixth embodiments of olefin polymerization catalysts of the invention are described.

[0116] The fifth olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I);

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair; and

a prepolymerized olefin polymer produced by prepolymerization.

[0117] The sixth olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I);

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair;

(C) an organoaluminium compound; and

a prepolymerized olefin polymer produced by prepolymerization.

[0118] Examples of the fine particle carrier used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those for the third and fourth olefin polymerization catalysts.

[0119] The transition metal compound (A) used for the fifth and sixth olefin polymerization catalysts of the invention is the same as that for the first and second olefin polymerization catalysts, and is represented by formula (I).

[0120] Examples of the organoaluminium oxy-compounds (B-1) used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for the first and second olefin polymerization catalysts.

[0121] Examples of the compounds (B-2) which react with the transition metal compound (A) to form an ion pair and used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for the first and second olefin polymerization catalysts.

[0122] Examples of the organoaluminium compounds (C) used for the sixth olefin polymerization catalyst of the invention are the same as those used for the second olefin polymerization catalyst.

[0123] Further, in the fifth and sixth olefin polymerization catalysts of the invention, water as described in the first and second olefin polymerization catalysts may be used as a catalyst component.

[0124] The fifth olefin polymerization catalyst of the invention can be prepared by prepolymerizing a small amount of an olefin to the solid catalyst component. The solid catalyst component is obtained by mixing the fine particle carrier, component (A) and component (B-1) (or component (B-2)), and if desired water, in an inert hydrocarbon medium (solvent) or an olefin medium (solvent). In the mixing of those components, component (C) can be further added.

[0125] There is no specific limitation on the order of mixing those components.

[0126] However, preferred processes are:

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)), and then with component (A), followed by mixing with water if desired

a process in which a mixture of component (B-1) (or component (B-2)) and component (A) is mixed and contacted with the fine particle carrier, followed by mixing with water if desired; and

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)) and water, followed by mixing with component (A).

[0127] The mixing of the components is desirably carried out with stirring.

[0128] In the mixing of each component, component (A) is usually used in an amount of 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, per 1 g of the fine particle carrier; and the concentration of component (A) is generally 5×10^{-6} to 2×10^{-2} mol/liter-medium, preferably 10^{-5} to 10^{-2} mol/liter-medium. The atomic ratio (Al:transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 3,000:1, preferably 20:1 to 2,000:1. When component (B-2) is used, the molar ratio (component (A):component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1.

[0129] When water is used as a catalyst component, the molar ratio (Al_{B-1}:H₂O) of aluminium atoms (Al_{B-1}) in component (B-1) to water (H₂O) is 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0130] The temperature for mixing the components is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact

time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0131] The fifth olefin polymerization catalyst of the invention can be prepared by prepolymerizing an olefin in the presence of the above-mentioned components. The prepolymerization can be carried out by introducing an olefin into an inert hydrocarbon medium (solvent) in the presence of the components and, if necessary, component (C).

[0132] In the prepolymerization, component (A) is usually used in an amount of 10^{-5} to 2×10^{-2} mol/liter, preferably 5×10^{-5} to 10^{-2} mol/liter. The prepolymerization temperature is -20 to 80 °C, preferably 0 to 50 °C; and the prepolymerization time is 0.5 to 100 hours, preferably about 1 to 50 hours.

[0133] The olefin used for the prepolymerization is selected from olefins which are used for polymerization. It is preferable to use the same monomer as used in the polymerization or a mixture of the same monomer as used in the polymerization and an α -olefin.

[0134] In the olefin polymerization catalyst of the invention obtained as above, it is desired that the transition metal atoms are supported in an amount of 10^{-6} to 10^{-3} g-atom, preferably 2×10^{-6} to 3×10^{-4} g-atom, per 1 g of the fine particle carrier; and the aluminium atom are supported in an amount of 10^{-3} to 10^{-1} g-atom, preferably 2×10^{-3} to 5×10^{-2} g-atom, per 1 g of the fine particle carrier. Further, it is also desired that component (B-2) is supported in an amount of 5×10^{-7} to 0.1 g-atom, preferably 2×10^{-7} to 3×10^{-2} g-atom, in terms of the boron atoms contained in component (B-2).

[0135] The amount of prepolymerized polymer prepared by the prepolymerization is desirably 0.1 to 500 g, preferably 0.3 to 300 g, particularly preferably 1 to 100 g, per 1 g of the fine particle carrier.

[0136] The sixth olefin polymerization catalyst of the invention is formed from the fifth olefin polymerization catalyst (component) and the organoaluminium compound (C). The organoaluminium compound (C) is used in an amount of not more than 500 mol, preferably 5 to 200 mol, per 1 g-atom of the transition metal atoms in the component (A).

[0137] The fifth and sixth olefin polymerization catalysts of the invention may contain other components useful for the olefin polymerization.

[0138] Examples of the inert hydrocarbon solvents used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for preparing the first and second olefin polymerization catalysts.

[0139] Polyolefins obtained by the use of the olefin polymerization catalysts as described above have a narrow molecular weight distribution, a narrow composition distribution and a high molecular weight and the olefin polymerization catalysts have a high polymerization activity.

[0140] Further, when olefins of 3 or more carbon atoms are polymerized in the presence of the olefin polymerization catalysts, polyolefins having excellent stereoregularity can be obtained.

[0141] Next, the process for olefin polymerization according to the present invention is described.

[0142] An olefin is polymerized in the presence of any of the above-described olefin polymerization catalysts. The polymerization may be carried out by a liquid phase polymerization process such as suspension polymerization or by a gas phase polymerization.

[0143] In the liquid phase polymerization process, the same inert hydrocarbon solvent as used in the preparation of the catalyst can be used, or the olefin itself can be also used as a solvent.

[0144] In the polymerization of an olefin using the first or second polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system.

[0145] In the polymerization of an olefin using the third or fourth polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system. In this case, an aluminosilicate which is not supported on the carrier may be employed, if desired.

[0146] In the polymerization of an olefin using the fifth or sixth polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system. In this case, an aluminosilicate which is not supported on the carrier may be employed, if desired.

[0147] In the slurry polymerization, the temperature for the olefin polymerization is usually -50 to 100 °C, preferably 0 to 90 °C. In the liquid phase polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization process, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The polymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the polymerization may be performed in two or more stages having different reaction conditions.

[0148] The molecular weight of the resulting olefin polymer can be regulated by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature.

[0149] Examples of the olefins to be polymerized using the olefin polymerization catalysts of the invention include:

α -olefins of 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and cycloolefins of 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.

[0150] Also employable are styrene, vinylcyclohexane or diene.

[0151] When the olefin polymerization catalyst of the invention is used to polymerize an α -olefin of 3 or more carbon atoms, a polymer having a lower melting point is obtainable as compared with a polymer obtained by using a conventional metallocene type catalyst, even though the polymers have the almost the same molecular weight. Further, when the catalyst of the invention is used, a copolymer having a low melting point can be obtained even if the amount of recurring units derived from a comonomer is small.

[0152] If an α -olefin of 3 or more carbon atoms is polymerized using the olefin polymerization catalyst of the invention, a large number of inversely inserted monomer units are present in the molecules of the resultant olefin polymer. It is known that in the α -olefin prepared by a polymerization of an α -olefin of 3 or more carbon atoms in the presence of a chiral metallocene catalyst, 2,1-insertion or 1,3-insertion takes place in addition to the ordinary 1,2-insertion, whereby an inversely inserted unit such as a 2,1-insertion or 1,3-insertion is formed in the olefin polymer molecule (see: Makromol. Chem., Rapid Commun., 8,305 (1987), by K. Soga, T. Shiono, S. Takemura and W. Kaminsky). It is also known that when inverse insertions are present in the olefin polymer molecule, the melting point of the olefin polymer becomes low for its stereoregularity (see: Polymer, 30, 1350 (1989), by T. Tsutsui, N. Ishimura, A. Mizuno, A. Toyota and N. Kashiwa).

[0153] In the molecule of the olefin polymer obtained by polymerizing an α -olefin of 3 or more carbon atoms using the olefin polymerization catalyst of the invention, a large number of inversely inserted monomer units are present, and hence it is presumed that the melting point of the olefin polymer is lower than the melting point of an olefin polymer having almost the same molecular weight which is obtained by the use of a conventional catalyst.

[0154] The catalyst of the present invention may be used to prepare a propylene polymer, propylene copolymer or propylene elastomer.

Propylene polymer

[0155] The propylene polymer comprises propylene units, but may also contain constituent units derived from other olefins in an amount of less than 0.5 % by mol, preferably less than 0.3 % by mol, more preferably less than 0.1 % by mol.

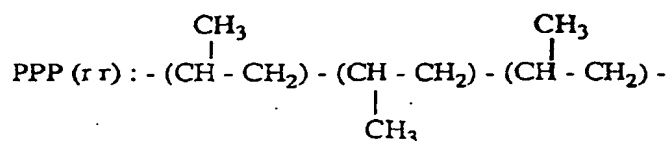
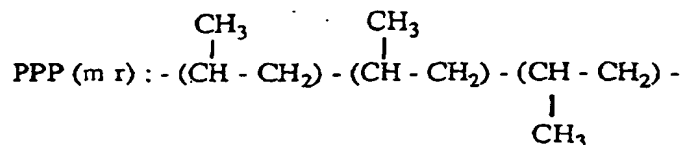
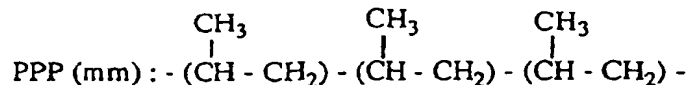
[0156] The propylene polymer has a triad tacticity of not less than 90 %, preferably not less than 93 %, more preferably not less than 95 %. The term "triad tacticity" means a proportion of chains of three propylene units (i.e., chains consisting of three propylene units continuously bonded) that the directions of methyl branches in the propylene chain are the same as each other and each propylene unit is bonded to each other with head-to-tail bonds, to total three propylene units-chains in the polymers. This term is sometimes referred to as "mm fraction" hereinafter.

[0157] The triad tacticity can be determined from a ^{13}C -NMR spectrum of the propylene polymer.

[0158] The ^{13}C -NMR spectrum is measured in the following manner. A 50 to 60 mg sample is completely dissolved in a mixed solvent containing about 0.5 ml of hexachlorobutadiene, o-dichlorobenzene or 1,2,4-trichlorobenzene and about 0.05 ml of deuterated benzene (i.e., lock solvent) in a NMR sample tube (diameter: 5 mm), and then subjected to a proton perfect decoupling method at 120 °C to measure the ^{13}C -NMR spectrum. The measurement is conducted under the conditions of a flip angle of 45° and a pulse interval of not less than 3.4 T_1 (T_1 is the maximum value with respect to the spin-lattice relaxation time of the methyl group). T_1 of the methylene group and T_1 of the methine group are each shorter than that of the methyl group, and hence the magnetization recovery of all carbons under these conditions is not less than 99 %.

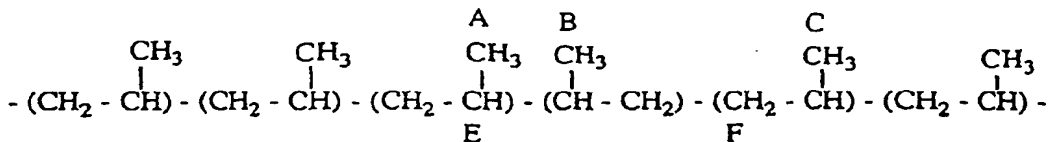
[0159] With respect to the chemical shift, the methyl group of the third unit in the 5 propylene units-chain consisting of head-to-tail bonds and having the same directions of the methyl branches is set to 21.593 ppm, and the chemical shifts of other carbon peaks are determined using the above-mentioned value as a reference. Accordingly, a peak based on the methyl group of the second unit in the three propylene units-chain having a PPP(mm) structure appears in the range of 21.1 to 21.8 ppm; a peak based on the methyl group of the second unit in the three propylene units-chain having a PPP(mr) structure appears in the range of 20.2 to 21.1 ppm; and a peak based on the methyl group of the second unit in the three propylene units-chain having PPP(rr) structure appears in the range of 19.4 to 20.2 ppm.

[0160] PPP(mm), PPP(mr) and PPP(rr) structures have the following 3 propylene units-chain structure with head-to-tail bonds, respectively.

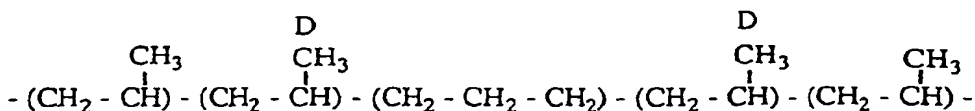


[0161] In addition to the ordered structures represented by PPP(mm), PPP(mr) and PPP(rr), the propylene polymer has a structure (i) containing an inversely inserted unit based on the 2,1-insertion and a structure (ii) containing an inversely inserted unit based on the 1,3-insertion, in small amounts.

Structure (i)



Structure (ii)



[0162] The aforementioned definition of the mm fraction is not applied to the propylene units having the carbons attached with marks A, B, C and D among the carbons attached with marks A to F. The carbon A and the carbon B resonate in the region of 16.5 to 17.5 ppm, the carbon C resonates in the vicinity of 20.8 ppm (mr region), and the carbon D resonates in the vicinity of 20.7 ppm (mr region). In the structure (i) and the structure (ii), however, not only the peak of the methyl group but also the peaks of the adjacent methylene and methine groups must be confirmed.

[0163] In the structure (ii), a $-(\text{CH}_2)_3-$ unit is produced and a unit corresponding to one methyl group disappears as a result of hydrogen transfer polymerization.

[0164] Accordingly, the mm fraction in all of the polymer chains can be represented by the following formula:

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$$\text{mm Fraction (\%)} = \frac{\text{area of methyl group (21.1 ~ 21.8 ppm)}}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100$$

5 wherein ΣI_{CH_3} denotes the total areas of all peaks derived from the methyl groups.

[0165] Further, $I_{\alpha\delta}$ and $I_{\beta\gamma}$ are an area of $\alpha\delta$ peak (resonance in the vicinity of 37.1 ppm) and an area of $\beta\gamma$ peak (resonance in the vicinity 27.3 ppm), respectively. Naming of these methylene peaks was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781).

10 [0166] In the polymerization to prepare a propylene polymer, the 1,2-insertion of the propylene monomer mainly takes place, but the 2,1-insertion or the 1,3-insertion thereof sometimes takes place. The 2,1-insertion forms the inversely inserted unit represented by structure (i) in the polymer chain. The proportion of the 2,1-propylene monomer insertions to all propylene insertions was calculated by the following formula.

$$15 \text{ Proportion of inversely inserted units based on 2,1-insertion (\%)} = \frac{0.5 \times \{\text{area of methyl group (16.5 ~ 17.5 ppm)}\}}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100$$

[0167] Likewise, the proportion of the 1,3-propylene monomer insertions represented by structure (ii) to all propylene insertions was calculated by the following formula.

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$$\begin{aligned} &\text{Proportion of inversely} \\ &\text{inserted units based} = \frac{(I_{\alpha\delta} + I_{\beta\gamma}) / 4}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100 \\ 25 &\text{on 3,1-insertion (\%)} \end{aligned}$$

The proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ^{13}C -NMR, is not less than 0.7 %, preferably 0.7 to 2.0 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion in all propylene insertions is not more than 0.05 %, preferably not more than 0.04 %, more preferably not more than 0.03 %.

30

[0168] The propylene polymer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dl/g, preferably 0.5 to 12 dl/g, more preferably 1 to 12 dl/g.

35

[0169] The propylene polymer is prepared by polymerizing propylene in the presence of the aforesaid olefin polymerization catalysts. The polymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization and a solution polymerization) or a gas phase polymerization.

[0170] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, or propylene can be also used as a solvent.

40

[0171] In the suspension polymerization, the temperature for polymerizing propylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The polymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the polymerization can be carried out in two or more stages having different reaction conditions.

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[0172] The molecular weight of the resultant propylene polymer can be regulated by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature and the polymerization pressure.

Propylene copolymer

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[0173] The propylene copolymer is a propylene/ethylene random copolymer containing propylene units in an amount of 95 to 99.5 % by mol, preferably 95 to 99 % by mol, more preferably 95 to 98 % by mol, and ethylene units in an amount of 0.5 to 5 % by mol, preferably 1 to 5 % by mol, more preferably 2 to 5 % by mol.

[0174] The propylene copolymer may contain constituent units derived from other olefins in an amount of not more than 5 % by mol.

55

[0175] In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds, as measured by ^{13}C -NMR, is not less than 90 %, preferably not less than 93 %, more preferably not less than 96 %.

[0176] The triad tacticity (mm fraction) of the propylene copolymer can be determined from a ^{13}C -NMR spectrum of the propylene copolymer and the following formula:

$$\text{mm Fraction} = \frac{\text{PPP(mm)}}{\text{PPP(mm)} + \text{PPP(mr)} + \text{PPP(rr)}}$$

wherein PPP(mm); PPP(mr) and PPP(rr) denote the peak areas derived from the methyl groups of the second units in the three propylene units-chains consisting of head-to-tail bonds as defined above.

[0177] The ^{13}C -NMR spectrum of the propylene copolymer can be measured in the same manner as described for the propylene polymer. The spectrum relating to the methyl carbon region (16 - 23 ppm) can be classified into the first region (21.1 - 21.9 ppm), the second region (20.3 - 21.0 ppm), the third region (19.5 - 20.3 ppm) and the fourth region (16.5 - 17.5 ppm). Each peak in the spectrum was assigned with reference to "Polymer", 30 (1989) 1350.

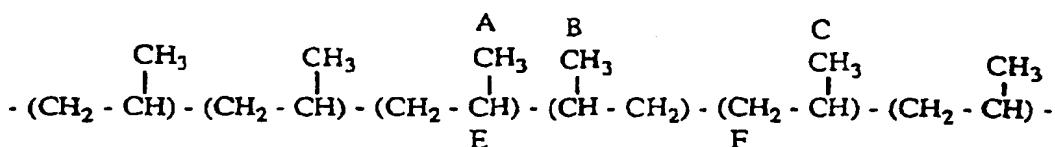
[0178] In the first region, the methyl group of the second unit in the three propylene units-chain represented by PPP (mm) resonates.

[0179] In the second region, the methyl group of the second unit in the three propylene units-chain represented by PPP(mr) resonates and the methyl group (PPE-methyl group) of a propylene unit whose adjacent units are a propylene unit and an ethylene unit resonates (in the vicinity of 20.7 ppm).

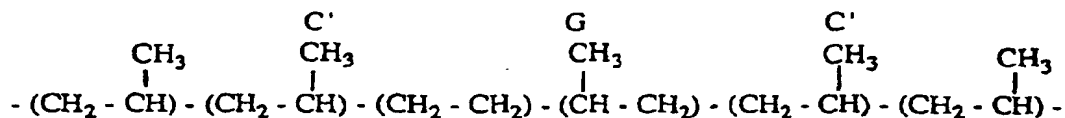
[0180] In the third region, the methyl group of the second unit in the three propylene units-chain represented by PPP (rr) resonates and the methyl group (EPE-methyl group) of a propylene unit whose adjacent units are ethylene units resonate (in the vicinity of 19.8 ppm).

[0181] Further, the propylene copolymer has the following structures (i) and (iii) containing an inversely inserted unit.

Structure (i)



Structure (iii)



[0182] Of the carbons attached with marks A to G, a peak of the carbon C and a peak of the carbon C' appear in the second region, a peak of the carbon G appears in the third region, and a peak of the carbon A and a peak of the carbon B appear in the fourth region.

[0183] Of the peaks which appear in the first to fourth regions as described above, peaks which are not based on the three propylene units-chain consisting of head-to-tail bonds are peaks based on the PPE-methyl group, the EPE-methyl group, the carbon C, the carbon C', the carbon G, the carbon A and the carbon B.

[0184] The peak area based on the PPE-methyl group can be evaluated by the peak area of the PPE-methine group (resonance in the vicinity of 30.6 ppm), and the peak area based on the EPE-methyl group can be evaluated by the peak area of the EPE-methine group (resonance in the vicinity of 32.9 ppm). The peak area based on the carbon C can be evaluated by 1/2 as much as the sum of the peak areas of the carbon F and the carbon E both having the inversely inserted structure (structure (i)) (resonance in the vicinity of 35.6 ppm and resonance in the vicinity of 35.4 ppm, respectively). The peak area based on the carbon C' can be evaluated by 1/2 as much as the sum of the peak areas of the $\alpha\beta$ methylene carbons having the inversely inserted structure (structure (iii)) (resonance in the vicinity of 34.3 ppm and resonance in the vicinity of 34.5 ppm, respectively). The peak area based on the carbon G can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.7 ppm).

[0185] Accordingly, by subtracting these peak areas from the total peak areas of the second region and the third region, the peak areas based on the three propylene units-chains (PPP(mr) and PPP(rr)) consisting of head-to-tail bonds can be obtained.

[0186] Since the positions of the carbon A peak and the carbon B peak have no concern with the peak of the three

propylene units-chain (PPP), they do not need to be taken into account.

[0187] Thus, the peak areas of PPP(mm), PPP(mr) and PPP(rr) can be evaluated, and hence the triad tacticity of the propylene unit chain consisting of head-to tail bonds can be determined.

[0188] In the propylene copolymer, the proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ^{13}C -NMR, is not less than 0.5 %, preferably 0.5 to 1.5 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer in all propylene insertions is not more than 0.05 %, preferably not more than 0.04 %, more preferably not more than 0.03 %.

[0189] In the polymerization, the 1,2-insertion of the propylene monomer (i.e., the methylene side is bonded to the catalyst) mainly takes place, but the 2,1-insertion thereof sometimes takes place. The 2,1-insertion forms the inversely inserted unit in the polymer.

[0190] The proportion of the 2,1-insertions to all propylene insertions in the propylene copolymer was calculated by the following formula with reference to "Polymer", 30 (1989) 1350.

Proportion of inversely inserted unit based on 2,1-insertion (%)

$$= \frac{0.5 I_{\alpha\beta}(\text{structure (i)}) + 0.25 I_{\alpha\beta}(\text{structure (iii)})}{I_{\alpha\alpha} + I_{\alpha\beta}(\text{structure (i)}) + 0.5(I_{\alpha\gamma} + I_{\alpha\beta}(\text{structure (iii)}) + I_{\alpha\delta})} \times 100$$

[0191] Naming of the peaks in the above formula was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781). $I_{\alpha\delta}$ denotes a peak area of the $\alpha\delta$ peak.

[0192] The proportion (%) of the amount of the three propylene units-chains based on the 1,3-insertion was determined by dividing 1/2 as much as the area of the $\beta\gamma$ peak (resonance in the vicinity of 27.4 ppm) by the sum of all the methyl group peaks and 1/2 as much as the $\beta\gamma$ peak, and then multiplying the resulting value by 100.

[0193] The propylene copolymer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dL/g, preferably 0.5 to 12 dL/g, more preferably 1 to 12 dL/g.

[0194] The propylene copolymer is prepared by copolymerizing propylene and ethylene in the presence of the aforesaid olefin polymerization catalysts. The copolymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization and a solution polymerization) or a gas phase polymerization.

[0195] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, and propylene and/or ethylene can be also used as a solvent.

[0196] In the suspension polymerization, the temperature for copolymerizing propylene and ethylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The copolymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The copolymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the copolymerization can be carried out in two or more stages having different reaction conditions.

[0197] The molecular weight of the resultant propylene copolymer can be regulated by allowing hydrogen to exist in the copolymerization system or by varying the copolymerization temperature and the copolymerization pressure.

Propylene elastomer

[0198] The propylene elastomer is a propylene/ethylene random copolymer containing propylene units in an amount of 50 to 95 % by mol, preferably 60 to 93 % by mol, more preferably 70 to 90 % by mol, and containing ethylene units in an amount of 5 to 50 % by mol, preferably 7 to 40 % by mol, more preferably 10 to 30 % by mol.

[0199] The propylene elastomer may contain constituent units derived from other olefins in an amount of not more than 10 % by mol.

[0200] In the propylene elastomer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds, as measured by ^{13}C -NMR, is not less than 90.0 %, preferably not less than 92.0 %, more preferably not less than 95.0 %.

[0201] The triad tacticity (mm fraction) of the propylene elastomer can be determined from a ^{13}C -NMR spectrum of the propylene elastomer and the following formula:

$$\text{mm Fraction} = \frac{\text{PPP(mm)}}{\text{PPP(mm)} + \text{PPP(mr)} + \text{PPP(rr)}}$$

wherein PPP(mm), PPP(mr) and PPP(rr) have the same meanings as above.

[0202] The ^{13}C -NMR spectrum of the propylene elastomer can be measured in the same manner as described for the propylene polymer. The spectrum relating to the methyl carbon region (19 - 23 ppm) can be classified into the first region (21.2 - 21.9 ppm), the second region (20.3 - 21.0 ppm) and the third region (19.5 - 20.3 ppm). Each peak in the

spectrum was assigned with reference to a literature "Polymer", 30 (1989) 1350.

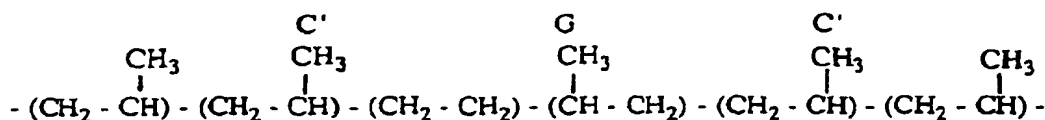
[0203] In the first region, the methyl group of the second unit in the three propylene units-chain represented by PPP (mm) resonates.

[0204] In the second region, the methyl group of the second unit in the three propylene units-chain represented by PPP(mr) resonates and the methyl group (PPE-methyl group) of a propylene unit whose adjacent units are a propylene unit and an ethylene unit resonates (in the vicinity of 20.7 ppm).

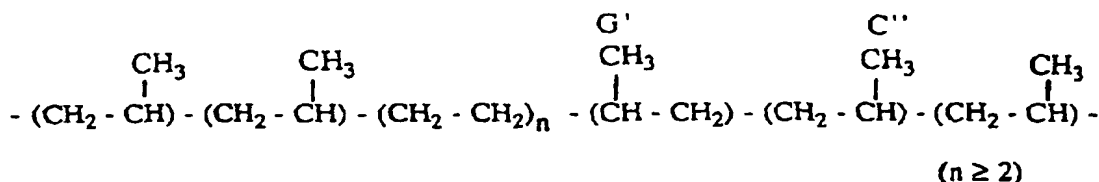
[0205] In the third region, the methyl group of the second unit in the three propylene units-chain represented by PPP (rr) resonates and the methyl group (EPE-methyl group) of a propylene unit whose adjacent units are ethylene units resonates (in the vicinity of 19.8 ppm).

[0206] Further, the propylene elastomer has the following structures (iii) and (iv) containing an inversely inserted unit.

Structure (iii)



Structure (iv)



[0207] Of the carbons attached with marks C and G, a peak of the carbon C' and a peak of the carbon C'' appear in the second region, and a peak of the carbon G and a peak of the carbon G' appear in the third region.

[0208] Of the peaks which appear in the first to third regions as described above, peaks which are not based on the 3 propylene units-chain consisting of head-to-tail bonds are peaks based on the PPE-methyl group, the EPE-methyl group, the carbon C', the carbon C'', the carbon G and the carbon G'.

[0209] The peak area based on the PPE-methyl group can be evaluated by the peak area of the PPE-methine group (resonance in the vicinity of 30.6 ppm), and the peak area based on the EPE-methyl group can be evaluated by the peak area of the EPE-methine group (resonance in the vicinity of 32.9 ppm). The peak area based on the carbon C' can be evaluated by twice as much as the peak area of the methine carbon (resonance in the vicinity of 33.6 ppm) to which the methyl group of the carbon G is directly bonded; and the peak area based on the carbon C'' can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.2 ppm) of the methyl group of the carbon G'. The peak area based on the carbon G can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.6 ppm); and the peak area based on the carbon G' can be also evaluated by the adjacent methine carbon (resonance in the vicinity of 33.2 ppm).

[0210] Accordingly, by subtracting these peak areas from the total peak areas of the second region and the third region, the peak areas based on the 3 propylene units-chains (PPP(mr) and PPP(rr)) consisting of head-to-tail bonds can be obtained.

[0211] Thus, the peak areas of PPP(mm), PPP(mr) and PPP(rr) can be evaluated, and hence the triad tacticity of the propylene unit chain consisting of head-to tail bonds can be determined.

[0212] In the propylene elastomer, the proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ¹³C-NMR, is not less than 0.5 %, preferably 0.5 to 2.0 %, more preferably 0.5 to 1.5 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion is not more than 0.05 %, more preferably 0.01 to 0.05 %.

preferably not more than 0.03 %.

[0213] The proportion of the 2,1-insertions to all of the propylene insertions in the propylene elastomer was calculated by the following formula with reference to "Polymer", 30 (1989) 1350.

Proportion of inversely inserted unit based on 2,1-insertion (%)

$$= \frac{0.25 I_{\alpha\beta}(\text{structure (iii)}) + 0.5 I_{\alpha\beta}(\text{structure (iv)})}{I_{\alpha\alpha} + I_{\alpha\beta}(\text{structure (iv)}) + 0.5 \{I_{\alpha\gamma} + I_{\alpha\beta}(\text{structure (iii)}) + I_{\alpha\delta}\}} \times 100$$

[0214] Naming of the peaks in the above formula was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781). $I_{\alpha\delta}$ denotes a peak area of the $\alpha\delta$ peak.

[0215] If it is difficult to determine the peak area of, for example, $I_{\alpha\delta}$ directly from the spectrum because of overlapping of the peaks, a carbon peak having a corresponding area can be substituted therefor.

[0216] The proportion (%) of the amount of the three propylene units-chains based on the 1,3-insertion was determined by dividing 1/2 as much as the area of the $\beta\gamma$ peak (resonance in the vicinity of 27.4 ppm) by the sum of all the methyl group peaks and 1/2 as much as the $\beta\gamma$ peak, and then multiplying the resulting value by 100.

[0217] The propylene elastomer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dl/g, preferably 0.5 to 12 dl/g, more preferably 1 to 12 dl/g.

[0218] The propylene elastomer is prepared by copolymerizing propylene and ethylene in the presence of the aforesaid olefin polymerization catalysts. The copolymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization or a solution polymerization) or a gas phase polymerization.

[0219] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, and propylene and/or ethylene can be also used as a solvent.

[0220] In the suspension polymerization, the temperature for copolymerizing propylene and ethylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The copolymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The copolymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the copolymerization can be carried out in two or more stages having different reaction conditions.

[0221] The molecular weight of the resultant propylene elastomer can be regulated by allowing hydrogen to exist in the copolymerization system or by varying the copolymerization temperature and the copolymerization pressure.

[0222] The novel transition metal compound according to the invention can be used as an olefin polymerization catalyst component.

[0223] The olefin polymerization catalyst of the invention has a high polymerization activity and polyolefins prepared by the use of the catalyst have a narrow molecular weight distribution and a narrow composition distribution. When an α -olefin of 3 or more carbon atoms is used, a polymer having a lower melting point is obtainable as compared with a polymer obtained by using a conventional metallocene catalyst even though the polymers have the almost the same molecular weight.

[0224] By the use of the catalyst of the invention, a copolymer having a low melting point can be obtained even if the amount of recurring units derived from a comonomer is small. Further, because of the small amount of solvent-soluble components, the resultant copolymer has excellent properties such as transparency, heat-sealing and anti-blocking. Moreover, the synthesis of polypropylene can be made with fewer reaction steps and is more economic, as compared with the synthesis using a conventional metallocene catalyst when polypropylene having almost the same molecular weight is produced.

[0225] When a copolymer elastomer mainly containing ethylene units and propylene units is prepared using the olefin polymerization catalyst of the invention, the resultant elastomer has a high molecular weight. Such a copolymer elastomer has a high strength, and hence when used as a modifier the elastomer exhibits excellent effects in the improvement of impact strength and hardness of polyolefins. When the copolymer elastomer is used to prepare a propylene block copolymer, the resultant copolymer is well-balanced between heat resistance, rigidity or transparency and impact strength because the molecular weight of the copolymer elastomer can be increased. Also in the preparation of polyethylene, the resultant polyethylene has excellent mechanical strength such as impact strength, tensile strength and flexural strength for the same reason.

[0226] The propylene polymer which can be prepared has excellent rigidity, heat resistance, surface hardness, glossiness, transparency and impact resistance. Hence, it can be suitably used for, for example, various industrial parts, containers, films, nonwoven fabrics, or stretched yarns.

[0227] The propylene copolymer which can be produced has excellent transparency, rigidity, surface hardness, heat resistance, heat-sealing properties, anti-blocking properties, bleed resistance and impact resistance. Hence, it can be suitably used for, for example, films, sheets, containers, stretched yarns or nonwoven fabrics.

[0228] The propylene elastomer which can be produced has excellent heat resistance, impact absorbing properties, transparency, heat-sealing properties and anti-blocking properties. Hence, it can be singly used for, for example, films or sheets, and moreover can be suitably used as a modifier of a thermoplastic resin.

5 EXAMPLES

[0229] The present invention is described in more detail in the following Examples.

[0230] The intrinsic viscosity $[\eta]$, molecular weight distribution (Mw/Mn), stereoregularity (mmmm), proportion of inversely inserted units, melting point (Tm) melt flow rate (MFR), flexural modulus (FR), heat distortion temperature (HDT), heat seal-starting temperature and heat seal-starting temperature after heat treatment, izod impact strength (IZ) and film impact strength are measured by the following methods.

Intrinsic viscosity $[\eta]$

[0231] The intrinsic viscosity $[\eta]$ was measured in decahydronaphthalene at 135 °C, and expressed as dl/g.

Molecular weight distribution (Mw/Mn)

[0232] The molecular weight distribution (Mw/Mn) was measured in the following manner using GPC-150C produced by Milipore Co.

[0233] A separation column of TSK-GNH-HT having a diameter of 72 mm and a length of 600 mm was used, and the column temperature was set to 140 °C. A sample (concentration 0.1 % by weight, amount: 500 microliters) was moved in the column at a rate of 1.0 ml/min using o-dichlorobenzene (available from Wako Junyaku Kogyo K.K.) as a mobile phase and 0.025 % by weight of BHT (Takeda Chemical Industries, Ltd.) as an antioxidant. A differential refractometer was used as a detector. Standard polystyrenes available from Toso Co., Ltd. were used for Mw < 1,000 and Mw > 4 × 10⁶, and polystyrenes available from Pressure Chemical Co. were used for 1,000 < Mw < 4 × 10⁶.

Stereoregularity (mm triad tacticity and mmmm pentad tacticity)

[0234] mm triad tacticity was measured as mentioned above.

[0235] mmmm pentad tacticity was measured as follows.

[0236] About 50 mg of a sample was completely dissolved in a mixed solvent containing 0.5 ml of o-dichlorobenzene (or hexachlorobutadiene) and 0.1 ml of deuterated benzene in a NMR sample tube (diameter: 5 mm) at about 120 °C, and then the ¹³C-NMR spectrum was measured (nuclear species: ¹³C, mode: perfect proton decoupling, temperature: 120 °C) by a GX500 type NMR measuring apparatus produced by Japan Electron Optics Laboratory Co., Ltd.

[0237] On the ¹³C-NMR spectrum, an area of a peak having resonance in the lowest magnetic field (21.8 ppm according to A. Zambelli, P. Locatelli, G. Bajo and F.A. Bovey, "Macromolecules", 8, 687 (1975)) was divided by a total area of all peaks of the methyl groups, and the resultant value was taken as a mmmm pentad tacticity value.

Proportion of inversely inserted units

[0238] For each of the polymers obtained in Examples 3 and 4 and Comparative Example 1, the proportions of the inversely inserted units based on the 2,1-insertion and the 1,3-insertion of a propylene monomer present in the propylene chain of the polymer were determined from the ¹³C-NMR spectrum and the following formulae.

$$2,1\text{-insertion (\%)} = \frac{0.5 \text{ } |\alpha\beta|}{|\alpha\alpha| + |\alpha\beta|} \times 100$$

$$1,3\text{-insertion (\%)} = \frac{0.5 \text{ } |\alpha\beta|}{|\alpha\alpha| + |\alpha\beta| + |\alpha\delta|} \times 100$$

wherein $|\alpha\alpha|$ is the total area of the $\alpha\alpha$ carbon peaks (resonances in the vicinity of 42.0 ppm and 46.2 ppm), $|\alpha\beta|$ is the total area of the $\alpha\beta$ carbon peaks (resonances in the vicinity of 30.2 ppm and 35.6 ppm), and $|\alpha\delta|$ is the area of the $\alpha\delta$ carbon peak (resonance in the vicinity of 37.1 ppm). Naming of the peaks (e.g., $\alpha\alpha$) was made in accordance with the classification by Carman, et al. (C.J. Carman and C.E. Wilkes, Rubber Chem. Technol., 44, 781 (1971)).

[0239] The proportions of the inversely inserted units in other Examples were measured by the method described before.

Melting point (T_m)

[0240] The melting point was determined from an endothermic curve given by heating about 5 mg of a sample charged in an aluminium pan to 200 °C at a rate of 10 °C/min, keeping it at 200 °C for 5 minutes, then cooling it to room temperature at a rate of 20 °C/min and heating it again at a rate of 10 °C/min. The measurement was conducted using a DSC-7 type apparatus produced by Perkin Elmer Co.

Melt flow rate (MFR)

[0241] The MFR is measured in accordance with ASTM D 1238 under a load of 2.16 kg at 230 °C.

Flexural modulus (FM)

[0242] The FM is measured in accordance with ASTM D 790 using a specimen of 12.7 mm (width) X 6.4 mm (thickness) X 127 mm (length) prepared by injection molding at a resin temperature of 200 °C and a molding temperature of 40 °C at a distance between spurs of 100 mm and a rate of flexing of 2 mm/min.

Heat distortion temperature (HDT)

[0243] The HDT is measured in accordance with ASTM D 648 under a load of 4.6 kg/cm².

Heat seal-starting temperature and heat seal-starting temperature after heat treatment

[0244] Using a T-die film having a width of 30 cm and a thickness of 50 µm prepared using a single screw extruder having a diameter of 30 mm under the conditions of a resin temperature of 210 °C (at a portion of die of extruder), a take-off speed of 3 m/min and a temperature of cooling roll of 25 °C, heat sealing of two films is carried out using a heat sealer by sealing at various seal temperatures under the conditions of a heat seal pressure of 2 kg/cm², a seal time of 1 second and a width of 5 mm, to prepare a sealed film. The above-prepared sealed film was allowed to cool.

[0245] The heat seal-starting temperature is defined as the temperature of the heat sealer when the peeling resistance of the sealed film becomes 300 g/25 mm, under such conditions that the sealed film is peeled off at 23 °C, a peeling speed of 200 mm/min and a peeling angle of 180 °.

[0246] Separately, another sealed film was subjected to heat treatment at 50 °C for 7 days. The heat seal-starting temperature after heat treatment was measured using the heat treated specimen.

Izod impact strength (IZ)

[0247] The IZ is measured in accordance with ASTM D 256 at 23 °C using a notched specimen of 12.7 mm (width) x 6.4 mm (thickness) X 64 mm (length).

[0248] The specimen is prepared by injection molding at a resin temperature of 200 °C and a molding temperature of 40 °C using a polypropylene composition obtained by dry-blending 20 % by weight of a polymer according to the present invention and 80 % by weight of a polypropylene (HIPOL™, grade J 700, melt flow rate: 11 g/10 min (at 230 °C), density: 0.91, manufactured by Mitsui petrochemical Industries, Ltd.), and melt-kneading at 200 °C using a twin-screw extruder.

Film impact strength

[0249] The film impact strength is measured using a film impact tester (manufactured by Toyo Seiki K.K., diameter of impact head bulb: 1/2 inch (12.7 mm φ)).

Example 1

Synthesis of rac-dimethylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride

Synthesis of 4-isopropyl-2,7-dimethylindene (compound 1)

[0250] A 1-liter reactor thoroughly purged with nitrogen was charged with 90 g (0.67 mol) of aluminium chloride and 150 ml of carbon disulfide, and to the reactor was dropwise added a solution of 47 ml (0.30 mol) of p-cymene and 33 ml (0.3 mol) of methacryloyl chloride in 30 ml of carbon disulfide at a temperature of 20 to 25 °C. The mixture was

reacted at room temperature for 12 hours and then added to 1 kg of ice, followed by extraction with ether. The obtained ether solution was washed with a saturated aqueous solution of sodium hydrogencarbonate and then water, and concentrated to obtain 68 g of an oil. This oil was purified by silica gel column chromatography (eluting solution: n-hexane) to obtain 42 g of a mixture (mixture 1) of 2,4-dimethyl-7-propyl-1-indanone and 2,7-dimethyl-4-isopropyl-1-indanone (yield: 67 %).

[0251] A 1-liter reactor thoroughly purged with nitrogen was charged with 2.82 g (0.075 mol) of lithium aluminium hydride and 200 ml of ether, and to the reactor was dropwise added a mixture of 36.5 g (0.18 mol) of the mixture 1 and 150 ml of ether while cooling with ice. After the dropwise addition was completed, the mixture was stirred at room temperature for 30 minutes and then refluxed for 1 hour. After the reaction was completed, the reaction mixture was worked up by a conventional procedure and then extracted with ether. The obtained ether solution was washed with a saturated aqueous solution of sodium hydrogencarbonate and water, and dried over sodium sulfate. The ether layer was concentrated to obtain 36 g of a solid. This solid was slurried in 100 ml of n-hexane and the solvent was evaporated off to obtain 30 g of a mixture (mixture No.2) of 2,4-dimethyl-7-isopropyl-1-indanol and 2,7-dimethyl-4-isopropyl-1-indanol (yield: 82 %).

[0252] A 1-liter reactor thoroughly purged with nitrogen was charged with 25 g (0.12 mol) of the mixture 2 and 500 ml of benzene. To the reactor was added 50 mg (0.55 mmol) of paratoluene sulfonic acid monohydrate, and the mixture was refluxed for 1 hour. After the reaction was completed, the reaction mixture was poured into 30 ml of saturated sodium hydrogencarbonate solution. The resulting organic layer was washed with water and then dried over anhydrous sodium sulfate. The organic layer was concentrated to give an oil which was then distilled to obtain 20 g of the title compound 1 (yield: 90 %).

[0253] The NMR data of the title compound 1 is shown in Table 1.

Synthesis of 1,1'-dimethylsilyl-bis(4-isopropyl-2,7-dimethylindene) (compound 2)

[0254] A 200-ml reactor thoroughly purged with nitrogen was charged with 9.5 g (51 mmol) of the title compound 1, 7.7 ml (51 mmol) of tetramethylethylenediamine and 60 ml of diethyl ether, followed by cooling to -10 °C. To the solution was added a solution of n-butyllithium (51 mmol) in hexane. After heating to room temperature, the solution was cooled again to -10 °C, 3.1 ml (25.5 mmol) of dimethyldichlorosilane was dropwise added over 30 minutes and the reaction was carried out for 1 hour. After the reaction was completed, the reaction solution was added to 40 ml of a saturated aqueous solution of ammonium chloride, then extracted with n-hexane, washed with water and dried over magnesium sulfate. The salt was removed, and the resulting organic layer was concentrated under reduced pressure to obtain a yellow oil which was purified by silica gel column chromatography (eluting solution: n-hexane) to obtain 5.4 g of the title compound 2 as a colorless amorphous product (yield: 50 %).

[0255] The NMR data of the title compound 2 is shown in Table 1.

Synthesis of rac-dimethylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride (compound 3)

[0256] A 300-ml reactor thoroughly purged with nitrogen was charged with 5.4 g (12.6 mmol) of the title compound 2 and 100 ml of tetrahydrofuran, and the content in the reactor was cooled to -78 °C and stirred. To the reactor was dropwise added 16 ml of n-butyllithium (a solution in n-hexane, 1.58 N, 25.2 mmol) over 20 minutes, and the mixture was stirred for another 1 hour keeping the temperature to prepare an anion solution which was then slowly heated to room temperature.

[0257] Separately, 100 ml of tetrahydrofuran was charged in a 300-ml reactor thoroughly purged with nitrogen, cooled to -78 °C and stirred. To the reactor was slowly added 2.94 g (12.6 mmol) of zirconium tetrachloride, followed by heating to room temperature. To the mixture was dropwise added the anion solution prepared above over 30 minutes, followed by stirring at room temperature for 12 hours. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and a solid precipitate was washed three times with 300 ml of hexane to remove insoluble substances. The obtained hexane solution was concentrated to about 50 ml, and the solution was cooled at 6 °C for 12 hours. ¹H-NMR analysis of the solid obtained, 1.78 g (yield: 24 %), showed that it was a mixture of a racemic modification and a mesoisomer (4 : 1). This mixture was recrystallized from 100 ml of hexane to obtain 0.22 g of the title compound 3 as a yellow prismatic crystal (yield: 3 %). The result of the FD mass spectrometry of the title compound 3 was 588 (M⁺).

[0258] The NMR data of the title compound 3 is shown in Table 1.

Example 2

Synthesis of rac-diphenylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride

Synthesis of 1,1'-diphenylsilyl-bis(4-isopropyl-2,7-dimethylindene) (compound 4)

[0259] The procedure of the synthesis of the title compound 2 in Example 1 was repeated except that 120 mg of copper cyanide was used in place of tetramethylethylenediamine and 5.7 ml of diphenyldichlorosilane in place of dimethyldichlorosilane.

[0260] The title compound 4 was obtained as a colorless amorphous product in an amount of 7.2 g (yield: 49 %).

[0261] The NMR data of the title compound 4 is shown in Table 1.

Synthesis of rac-diphenylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride (compound 5)

[0262] The procedure of the synthesis of the title compound 3 in Example 1 was repeated except that 7.1 g (12.9 mmol) of the title compound 4 was used in place of the title compound 2 and 3.01 of zirconium tetrachloride in place of 2.94 g.

[0263] The title compound 5 was obtained as an yellow prismatic crystal in an amount of 1.10 g (yield: 12 %). The result of the FD mass spectrometry of the compound 5 was 712 (M⁺).

[0264] The NMR data of the title compound 5 is shown in Table 1.

Table 1

NMR Data	
Compound No.	¹ H-NMR Spectrum (CDCl ₃ , ppm)
1	1.26(6H, d, J=7.2Hz), 2.70(3H, s), 2.38(3H, s), 2.88(1H, q, J=7.0Hz), 3.27(2H, s), 6.54(1H, s), 6.90(1H, s), 7.10(1H, s)
2	1.60(12H, d, J=7.2Hz), 0.94~1.14(6H, m), 1.91~2.06(6H, m), 2.26(6H, s), 2.71(2H, q, J=7.2Hz), 3.49(2H, s), 6.49(2H, s), 6.74(2H, s), 7.06(2H, s)
3	1.20(12H, d, J=7.2Hz), 1.29(6H, s), 2.21(6H, s), 2.33(6H, s), 2.81(2H, q, J=7.0Hz), 6.70(2H, s), 7.01(2H, s), 7.26(2H, s)
4	1.06(6H, d, J=7.2Hz), 1.26(6H, d, J=7.2Hz), 1.80(3H, s), 2.10(6H, s), 2.24(3H, s), 2.80(2H, s), 4.36(4H, br.s), 6.16(2H, s), 6.60-7.68(14H, m)
5	0.92(12H, d, J=6.8Hz), 2.02(6H, s), 2.36(6H, s), 2.60(2H, q, J=6.8Hz), 6.80(2H, s), 6.90(2H, s), 6.99(2H, s), 7.45-7.50(6H, m), 8.12-8.16(4H, m)

Example 3

[0265] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triisobutylaluminum, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropyl-1-indenyl)}zirconium dichloride to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0266] The amount of the polymer obtained was 158 g and the polymerization activity was 158 kg-PP/mmol-Zr. The polymer had an [η] of 4.55 dl/g, a Mw/Mn of 2.2, an mmmm pentad value of 95.5 %, a proportion of the 2,1-insertion of 0.90 % and a Tm of 147 °C.

Example 4

[0267] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triethylaluminum, 0.001 mmol (in terms of Zr atoms) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride and 0.002 mmol (in terms of B atoms) of tris(pentafluorophenyl)boron to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0268] The amount of the polymer obtained was 94 g and the polymerization activity was 94 kg-PP/mmol-Zr. The

polymer had an $[\eta]$ of 4.75 dl/g, a Mw/Mn of 2.3, an mmmm pentad value of 96.4 %, a proportion of the 2,1-insertion of 0.80 % and a Tm of 148 °C.

Comparative Example 1

[0269] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triisobutylaluminium, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2-methyl-4-isopropylindenyl)}zirconium dichloride to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0270] The amount of the polymer obtained was 125 g and the polymerization activity was 125 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 3.47 dl/g, a Mw/Mn of 2.1, an mmmm pentad value of 96.2 %, a proportion of the 2,1-insertion of 0.40 % and a Tm of 152 °C.

Example 5

[0271] A 1-liter glass reactor thoroughly purged with nitrogen was charged with 500 ml of toluene, and propylene was fed at a rate of 100 liters/hr, followed by warming to 50 °C. To the reactor was added a solution obtained by precontacting 3.5 mmol of methylaluminoxane and 0.01 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride in toluene, to polymerize propylene at 50 °C for 20 minutes. After the polymerization, the solution was poured into a methanol-hydrochloric acid solution, and the resulting mixture was filtered to give a polymer which was dried at 80 °C for 10 hours.

[0272] The amount of the polymer obtained was 32.6 g and the polymerization activity was 8.2 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 1.37 dl/g, a Mw/Mn of 2.2 and a Tm of 148 °C.

Comparative Example 2

[0273] The procedures of Example 5 were repeated except that rac-ethylenebis {1-(2, 4, 7-trimethylindenyl)} zirconium dichloride was used in place of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride.

[0274] The amount of the polymer obtained was 23.1 g and the polymerization activity was 5.8 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 0.44 dl/g, a Mw/Mn of 2.3 and a Tm of 150 °C. This polymer had a molecular weight which was much lower than that of the polymer obtained in Example 5.

Example 6

Preparation of solid catalyst component (a)

[0275] A 500-ml reactor thoroughly purged with nitrogen was charged with 25 g of silica (F-948, available from Fuji Devision Co.) which had been dried at 200 °C for 6 hours in a stream of nitrogen and 310 ml of toluene, and the system was set to 0 °C with stirring. To the system was dropwise added 90 ml of an organoaluminium oxy-compound (methylaluminoxane available from Schering Co., diluted in toluene, 2.1 mol/liter) over 60 minutes in a nitrogen atmosphere. Then, the mixture was reacted at the same temperature for 30 minutes and further at 90 °C for 4 hours. The reaction system was allowed to cool and when the temperature reached 60 °C, the supernatant was decanted off and the residue was washed three times with 150 ml of toluene at room temperature to obtain a solid catalyst component (a) containing 6.8 mmol of Al per 1 g of silica.

Preparation of solid catalyst component (b)

[0276] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.9 mmol of triisobutylaluminium were successively added to the reactor and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to prepolymerize propylene. The supernatant was decanted off and then the residue washed three times with 150 ml of toluene to obtain a solid catalyst component (b) in which Zr and Al were supported in amounts of 0.011 mmol and 4.48 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0277] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 3.6 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atom) of the solid catalyst component (b), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0278] The amount of the polymer (powder) obtained was 75 g, the amount (SP) of the polymer dissolved in the solvent was 1.9 g (2.5 % by weight), and the polymerization activity was 38.5 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 6.0 dg/min, a Mw/Mn of 2.6, an ethylene content of 2.9 % by mol and a Tm of 126 °C.

Example 7Preparation of solid catalyst component (c)

[0279] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis(1-(2,7-dimethyl-4-isopropylindenyl))zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.9 mmol of triisobutylaluminium were successively added to the reactor, and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to polymerize propylene. The supernatant was decanted off, and then the residue was washed three times with 150 ml of toluene to obtain a solid catalyst component (c) in which Zr and Al were supported in amounts of 0.011 mmol and 4.55 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0280] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 3.6 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atom) of the solid catalyst component (c), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0281] The amount of the polymer (powder) obtained was 59 g, the amount (SP) of the polymer dissolved in the solvent was 2.5 g (4.0 % by weight), and the polymerization activity was 30.7 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 5.8 dg/min, a Mw/Mn of 2.6, an ethylene content of 2.9 % by mol and a Tm of 127 °C.

Comparative Example 3Preparation of solid catalyst component (d)

[0282] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis(1-(2-methyl-4-isopropylindenyl))zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.09 mmol of triisobutylaluminium were successively added to the reactor, and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to prepolymerize propylene. The supernatant was decanted off, and then the residue was washed three times with 150 ml of toluene to obtain a solid catalyst component (d) in which Zr and Al were supported in amounts of 0.011 mmol and 4.35 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0283] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 5.2 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atoms) of the solid catalyst component (d), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0284] The amount of polymer (powder) obtained was 67 g, and a small amount of the polymer adhered to the autoclave wall was observed. The amount (SP) of the polymer dissolved in the solvent was 9.0 g (12.0 % by weight). The polymerization activity was 38 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 12 dg/min, a Mw/Mn of 2.5, an ethylene content of 5.0 % by mol and a Tm of 127 °C.

[0285] When the above polymerization procedure is performed in an industrial scale, it is presumed that the polymer which adheres to the autoclave wall will cause a reduced heat transfer efficiency, and that the high SP value will cause not only a reduced polymer yield but also an increased viscosity of the solvent removed, resulting in difficult operation.

Example 8

[0286] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene. The temperature of the autoclave was elevated to 40 °C, and to the autoclave were added 0.2 mmol of triisobutylaluminum, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)} zirconium dichloride, to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours under a reduced pressure.

[0287] The amount of the propylene polymer obtained was 158 g, and the polymerization activity was 158 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity $[\eta]$ of 4.55 dl/g. In the propylene polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.4 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.87 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.03 %.

[0288] The polymer had a melt flow rate (MFR) of 12.5 g/10 min, a flexural modulus (FM) of 12500 kg/cm², and a heat distortion temperature of 105 °C.

Example 9

[0289] 750 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 2.9 % by mol). To the reaction system were added 0.25 mmol of triisobutylaluminum, 0.5 mmol of methylaluminoxane and 0.0015 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)} zirconium dichloride, and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour while keeping the total pressure at 2 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 80 °C for 10 hours under a reduced pressure.

[0290] The amount of the propylene copolymer obtained was 26.9 g, and the polymerization activity was 17.9 kg-polymer/mmol-Zr. The copolymer had an intrinsic viscosity $[\eta]$ of 2.2 dl/g and an ethylene content of 3.0 % by mol. In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 97.3 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.9 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was 0.04 %.

[0291] The film of the copolymer had heat seal-starting temperature of 118 °C and a heat seal-starting temperature after heat treatment of 120 °C.

[0292] The results are shown in Table 2.

Example 10

[0293] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and 1 mmol of triisobutylaluminum was added thereto. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a pressure of 1.5 kg/cm², and propylene was then fed to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.3 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)} zirconium dichloride to polymerize the monomers for 20 minutes while propylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 110 °C for 10 hours under a reduced pressure.

[0294] The amount of the propylene copolymer obtained was 21.2 g, and the polymerization activity was 21 kg-polymer/mmol-Zr. The copolymer had an intrinsic viscosity $[\eta]$ of 1.5 dl/g and an ethylene content of 4.7 % by mol. In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 96.9 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 1.1 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.04 %.

[0295] The film of the copolymer had a heat seal-starting temperature of 107 °C and a heat seal-starting temperature

after heat treatment of 111 °C.

[0296] The results are shown in Table 2.

Example 11

[0297] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen. Then, to the autoclave was added 1 mmol of triisobutylaluminium and was fed 60 liters of propylene gas. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.45 mmol of methylaluminoxane and 0.0015 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride to polymerize the monomers for 40 minutes while ethylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol, and dried at 110 °C for 10 hours under reduced pressure.

[0298] The amount of the polymer obtained was 47.2 g. The polymerization activity was 31.5 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity [η] of 2.0 dl/g and an ethylene content of 27.0 % by mol. In the polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.4 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.88 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.05 %.

[0299] The film of the copolymer had a film impact strength of 6000 kgf-cm/cm, and the composition with polypropylene had IZ of 35 kg-cm/cm and a melt flow rate (MFR) of 9.3 g/10 min.

[0300] The results are shown in Table 2.

Example 12

[0301] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and 1 mmol of triisobutylaluminium was added thereto. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a pressure of 2.0 kg/cm², and then propylene was fed to the system to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.3 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride, to polymerize the monomers for 10 minutes while propylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 110 °C for 10 hours under reduced pressure.

[0302] The amount of the polymer obtained was 16.8 g and the polymerization activity was 16.8 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity [η] of 1.7 dl/g and an ethylene content of 8.5 % by mol. In the polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.6 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.62 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.05 %.

[0303] The film of the copolymer had a heat seal-starting temperature of 90 °C and a heat seal-starting temperature after heat treatment of 93 °C.

[0304] The results are shown in Table 2.

Table 2

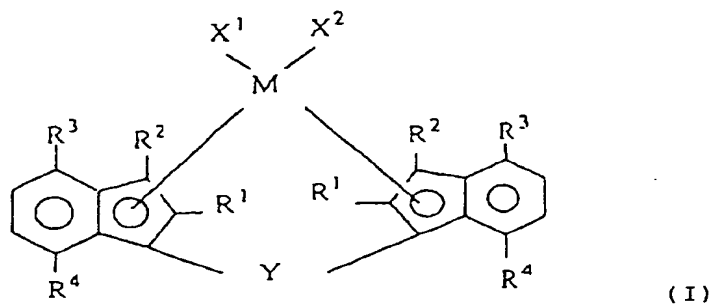
Example	Intrinsic viscosity [η]	Melt- ing point (°C)	Ethylene content (mol %)	Heat seal- starting tempera- ture (°C)	Heat seal- starting tempera- ture after heat treatment	Film impact strength (kg·cm /cm)
Ex. 9	2.2	120	3	118	120	-
Ex. 10	1.5	110	4.7	107	111	-
Ex. 11	2	-	27	-	-	6000
Ex. 12	1.7	90	8.5	90	93	-

Table 2 (Continued)

Example	IZ of composition with polypropylene (kgf·cm/cm)	MFR of composition with polypropylene (g/10 min)
Ex. 9	-	-
Ex. 10	-	-
Ex. 11	35	9.3
Ex. 12	-	-

Claims

1. A transition metal compound of formula (I):



wherein

M is zirconium;

R¹ and R², which may all be identical or different from each other, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms;

R³ is an isopropyl group;

R⁴ is a methyl group;

X¹ and X², which may be identical or different, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms; and

Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylarylsilylene group and an arylsilylene group.

2. An olefin polymerization catalyst comprising:

(A) a transition metal compound of formula (I) as defined in claim 1; and

(B) at least one compound selected from:

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

3. An olefin polymerization catalyst according to claim 2 which further comprises

(C) an organoaluminium compound.

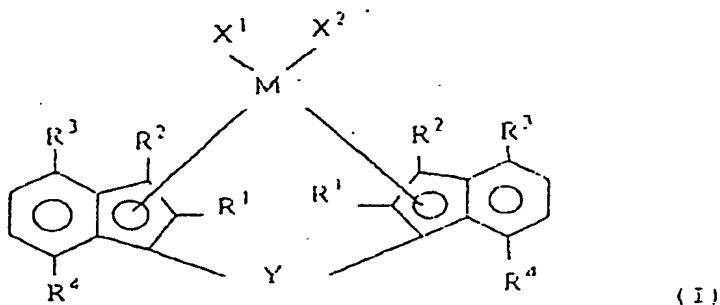
4. An olefin polymerization catalyst according to claim 2 or 3 which further comprises a fine particle carrier, components (A) and (B) being supported on said carrier.

5. An olefin polymerization catalyst according to claim 2 or 3 which further comprises a fine particle carrier and a prepolymerized olefin polymer produced by prepolymerization.

6. A process for olefin polymerization comprising polymerizing or copolymerizing an olefin in the presence of an olefin polymerization catalyst as defined in any one of claims 2 to 5.

Patentansprüche

1. Übergangsmetallverbindung der Formel (I):



worin M Zirkonium ist;

R¹ und R², die alle identisch oder voneinander verschieden sein können, jeweils ein Wasserstoffatom, ein Halogenatom oder eine Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen sind;

R³ eine Isopropylgruppe ist;

R⁴ eine Methylgruppe ist;

X¹ und X², die alle identisch oder voneinander verschieden sein können, jeweils ein Wasserstoffatom, ein Halogenatom oder eine Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen sind; und

Y eine zweiwertige Silicium enthaltende Gruppe ist, gewählt aus einer Alkylsilylengruppe, einer Alkylarylsilylengruppe und einer Arylsilylengruppe.

2. Olefin-Polymerisationskatalysator, umfassend:

(A) eine Übergangsmetallverbindung der Formel (I), wie in Anspruch 1 definiert; und

(B) mindestens eine Verbindung, gewählt aus:

(B-1) einer Organoaluminiumoxyverbindung und

(B-2) einer Verbindung, die mit der Übergangsmetallverbindung der Formel (I) reagiert unter Bildung eines Ionenpaares.

3. Olefin-Polymerisationskatalysator gemäß Anspruch 2, weiterhin umfassend:

(C) eine Organoaluminiumverbindung.

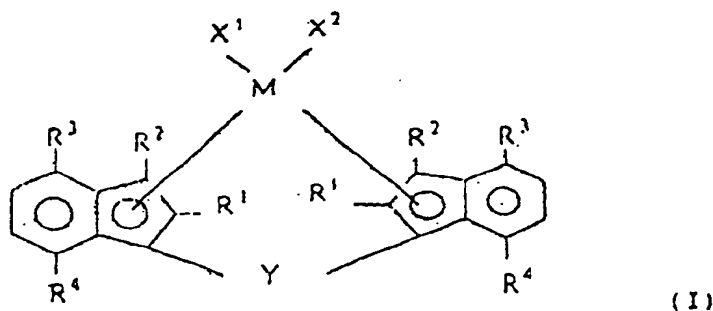
4. Olefin-Polymerisationskatalysator gemäß Anspruch 2 oder 3, weiterhin umfassend einen Feinteilchenträger, wobei die Komponenten (A) und (B) auf dem Träger getragen werden.

5. Olefin-Polymerisationskatalysator gemäß Anspruch 2 oder 3, weiterhin umfassend einen Feinteilchenträger und ein durch Prepolymerisation erzeugtes prepolymerisiertes Olefinpolymer.

6. Verfahren für die Olefin-Polymerisation, umfassend das Polymerisieren oder Copolymerisieren eines Olefins in Gegenwart eines Olefin-Polymerisationskatalysators, wie in mindestens einem der Ansprüche 2 bis 5 definiert.

Revendications

1. Dérivé de métal de transition de formule (I) :



dans laquelle M représente un atome de zirconium,

R¹ et R² qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné ayant 1 à 20 atomes de carbone,

R³ représente un groupe isopropyle,

R⁴ représente un groupe méthyle,

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X¹ et X² qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné ayant 1 à 20 atomes de carbone, et

Y représente un groupe divalent renfermant du silicium, choisi parmi les groupes alkylsilylène, les groupes alkylarylsilylène et les groupes arylsilylène.

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2. Catalyseur de polymérisation des oléfines, qui comprend :

(A) un dérivé de métal de transition de formule (I) tel que défini dans la revendication 1, et

(B) au moins un composé choisi parmi :

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(B-1) les composés organoaluminium du type oxy, et

(B-2) les composés qui réagissent avec le dérivé de métal de transition de formule (I) pour former une paire d'ions.

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3. Catalyseur de polymérisation des oléfines selon la revendication 2, qui renferme en outre

(C) un composé organoaluminium.

4. Catalyseur de polymérisation des oléfines selon la revendication 2 ou 3, qui comprend en outre un support en fines particules, les constituants (A) et (B) étant fixés sur ledit support.

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5. Catalyseur de polymérisation des oléfines selon la revendication 2 ou 3, qui comprend en outre un support en fines particules et un polymère d'oléfine prépolymérisée, produit par prépolymérisation.

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6. Procédé de polymérisation des oléfines, qui comprend la polymérisation ou la copolymérisation d'une oléfine en présence d'un catalyseur de polymérisation des oléfines, tel que défini dans l'une quelconque des revendications 2 à 5.

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(19)



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(11) **EP 0 629 631 B1**

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(22) Date of filing: **06.06.1994**

(54) **Novel transition metal compound, and polymerization catalyst containing it**

Übergangsmetallverbindung, und diese enthaltender Polymerisationskatalysator

Nouvelle composé métallique de transition, et catalyseur de polymérisation le contenant

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(56) References cited:
EP-A- 0 251 771 **EP-A- 0 374 695**
EP-A- 0 537 686

- **ANGEWANDTE CHEMIE. INTERNATIONAL**
EDITION, vol.31, no.10, October 1992,
WEINHEIM DE, XP000319626 W.SPALECK 'High
Molecular Weight Polypropylene through
Specifically Designed Zirconocene Catalysts'

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Description

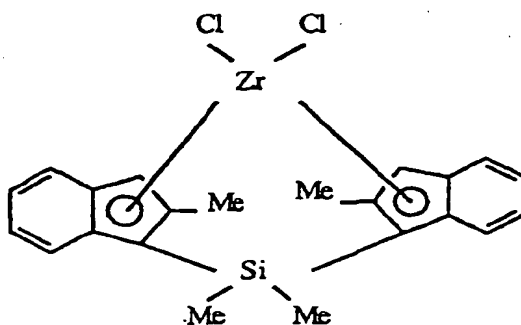
[0001] The present invention relates to a novel transition metal compound, an olefin polymerization catalyst comprising the transition metal compound, and a process for olefin polymerization using the olefin polymerization catalyst.

[0002] A well known homogeneous catalyst is, for example, the so-called Kaminsky catalyst. Use of this Kaminsky catalyst produces a polymer having an extremely high polymerization activity and a narrow molecular weight distribution.

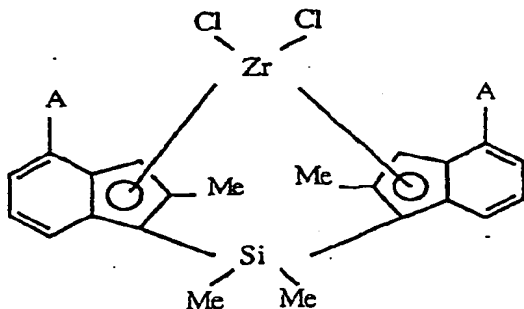
[0003] Of the Kaminsky catalysts, ethylenebis(indenyl)-zirconium dichloride and ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride are known as transition metal compounds for preparing isotactic polyolefins, as described in JP-A-130314/1986. However, polyolefins prepared by the use of these catalysts generally have a low stereoregularity and a low molecular weight. To prepare polyolefins of high stereoregularity and high molecular weight using these catalysts, the polymerization may be conducted at a low temperature, but this has a problem of low polymerization activity.

[0004] It is known that use of hafnium compounds in place of the zirconium compounds makes it possible to prepare a polymer having a high molecular weight, as described in Journal of Molecular Catalysis, 56 (1989), pp. 237-247, but this process also has a problem of low polymerization activity. Dimethylsilyl bisubstituted cyclopentadienyl zirconium dichloride is also known and described in JP-A-301704/1989 and Polymer Preprints, Japan, vol. 39, No. 6, pp. 1,614-1,616 (1990), but this compound is not satisfactory in all of polymerization activity, and stereoregularity and molecular weight of polymers obtained.

[0005] In order to solve these problems, various proposals have been made. For example, JP-A- 268307/1993 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane capable of preparing a high molecular weight polyolefin, but the molecular weight of the resultant polyolefin is still insufficient.



[0006] Further, EP-A-530 648 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane.

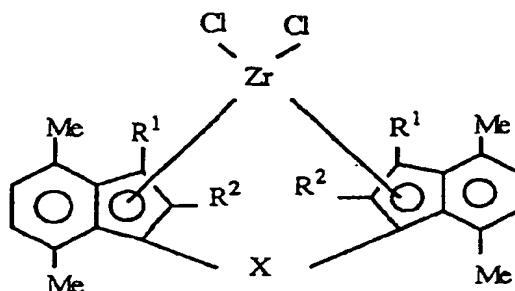


wherein A is a lower alkyl group.

[0007] The molecular weight of the polyolefin obtained by the use of this catalyst is high and industrially satisfactory.

In addition, since the melting point of the polyolefin (e.g., polypropylene) having high stereoregularity becomes high, the catalyst is suitably used for preparing a stereoregular polyolefin having a high melting point. However, it is unsuitable for preparing a stereoregular polyolefin (particularly a copolymer) having a high molecular weight and a low melting point, and the resultant polyolefin or copolymer does not have satisfactory qualities.

[0008] Furthermore, EP-A-537 686 describes an olefin polymerization catalyst formed from a metallocene compound of the following formula and an aluminoxane.



wherein R^1 and R^2 are each a methyl group or hydrogen, and X is a $\text{Si}(\text{CH}_3)_2$ group or an ethylene group.

[0009] However, a polyolefin obtained by the use of this catalyst has a low molecular weight and cannot be practically used.

[0010] Under the circumstances mentioned above, an olefin polymerization catalyst and a process for olefin polymerization, both having high olefin polymerization activity and being capable of preparing a polyolefin of excellent properties, are desired. The present inventors have found that the above requirements are satisfied by a transition metal compound which has two indenyl groups having a specific substituent group, said two indenyl groups being linked by, for example, a hydrocarbon group or a silicon-containing group.

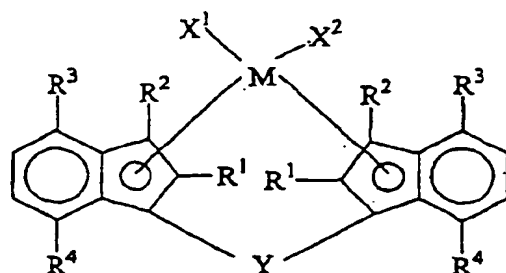
[0011] Propylene polymers have been applied to various uses because of their excellent mechanical properties and optical properties. For example, a propylene homopolymer has excellent rigidity, surface hardness, heat resistance, glossiness and transparency, and hence it is used for various industrial parts, containers, films and nonwoven fabrics. A propylene/ethylene random copolymer containing a small amount of ethylene units has excellent transparency, rigidity, surface hardness, heat resistance and heat-sealing properties, and hence is used for, for example, films or containers. A propylene elastomer has excellent impact absorbing properties, heat resistance and heat-sealing properties, and hence is singly used for films or used as a modifier of a thermoplastic resin.

[0012] However, the conventional propylene polymer does not always have sufficient transparency and impact resistance for some uses, and therefore a propylene polymer having excellent rigidity, heat resistance, surface hardness, glossiness, transparency and impact strength is desired. The conventional propylene/ethylene random copolymer does not always have sufficient transparency, heat-sealing properties, anti-blocking properties, bleed resistance and impact strength for some uses, and therefore a propylene/ethylene random copolymer having excellent transparency, rigidity, surface hardness, heat resistance and heat-sealing properties is desired. The conventional propylene elastomer does not always have sufficient heat-sealing properties, anti-blocking properties and heat resistance when used singly, and does not always have a sufficient effect of improving the impact resistance when used as a modifier. Therefore, a propylene elastomer having excellent impact resistance, heat resistance, transparency, heat-sealing properties, anti-blocking properties and effect of improving impact resistance is desired.

[0013] The present inventors have found that a propylene polymer, propylene copolymer and propylene elastomer which can be prepared by the use of an olefin polymerization catalyst containing the aforesaid specific transition metal compound as a catalyst component have the excellent properties mentioned above.

[0014] The present invention seeks to provide a transition metal compound useful for an olefin polymerization catalyst component having a high olefin polymerization activity.

[0015] The present invention provides a transition metal compound of formula (I):



wherein M is zirconium;

R¹ and R², which may all be identical or different from each other, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms;

R³ is an isopropyl group;

R⁴ is a methyl group;

X¹ and X², which may be identical or different, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms; and

Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylaryl silylene group and an arylsilylene group.

[0016] The present invention also provides an olefin polymerization catalyst comprising:

(A) a transition metal compound of formula (I); and

(B) at least one compound selected from:

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

[0017] The olefin polymerization catalyst may further comprise:

(C) an organoaluminium compound.

[0018] The olefin polymerization catalyst may also further comprise a fine particle carrier, components (A) and (B) being supported on said carrier.

[0019] The olefin polymerisation catalyst alternatively may also further comprise a fine particle carrier and a pre-polymerized olefin polymer produced by pre-polymerization.

[0020] The present invention also provides a process for olefin polymerization comprising polymerizing or copolymerizing an olefin in the presence of an olefin polymerization catalyst as defined above.

[0021] The olefin polymerization catalysts of the invention have high polymerization activity and an olefin polymer obtained by using the catalysts has a narrow molecular weight distribution and a narrow composition distribution. When they are used for polymerizing an α -olefin of 3 or more carbon atoms, a polymer having a lower melting point as compared with a polymer obtained by using a conventional metallocene catalyst, when these polymers have similar molecular weights, can be obtained. Further, in the preparation of a copolymer elastomer containing ethylene or propylene as its major component, a polymer of high molecular weight can be obtained.

[0022] When such catalysts are used, a copolymer having a low melting point can be obtained even though the amount of comonomer units may be small.

[0023] Fig. 1 illustrates the steps of a process for preparing the first and second embodiments of olefin polymerization catalysts of the invention.

[0024] Fig. 2 illustrates the steps of a process for preparing the third and fourth embodiments of olefin polymerization catalysts of the invention.

[0025] Fig. 3 illustrates the steps of a process for preparing the fifth and sixth embodiments of olefin polymerization catalysts of the invention.

[0026] In formula (I), M is zirconium.

[0027] R¹ and R² are each independently a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms.

[0028] Examples of the halogen atoms include fluorine, chlorine, bromine and iodine.

[0029] Examples of the hydrocarbon groups of 1 to 20 carbon atoms include an alkyl group such as methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, icosyl, norbornyl and adamantyl; an alkenyl group such as vinyl, propenyl and cyclohexenyl; an arylalkyl group such as benzyl, phenylethyl and phenylpropyl; and an aryl group such as phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthracenyl and phenanthryl.

[0030] Of these, R¹ is preferably a hydrocarbon group, particularly a hydrocarbon group of 1 to 3 carbon atoms such as methyl, ethyl and propyl. R² is preferably a hydrogen atom or a hydrocarbon group, particularly a hydrogen atom or a hydrocarbon group of 1 to 3 carbon atoms such as methyl, ethyl and propyl.

[0031] R³ is an isopropyl group and R⁴ is a methyl group.

[0032] X¹ and X² are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms. Examples of those atoms and groups include the halogen atoms and the hydrocarbon groups of 1 to 20 carbon atoms exemplified above with respect to R¹ and R².

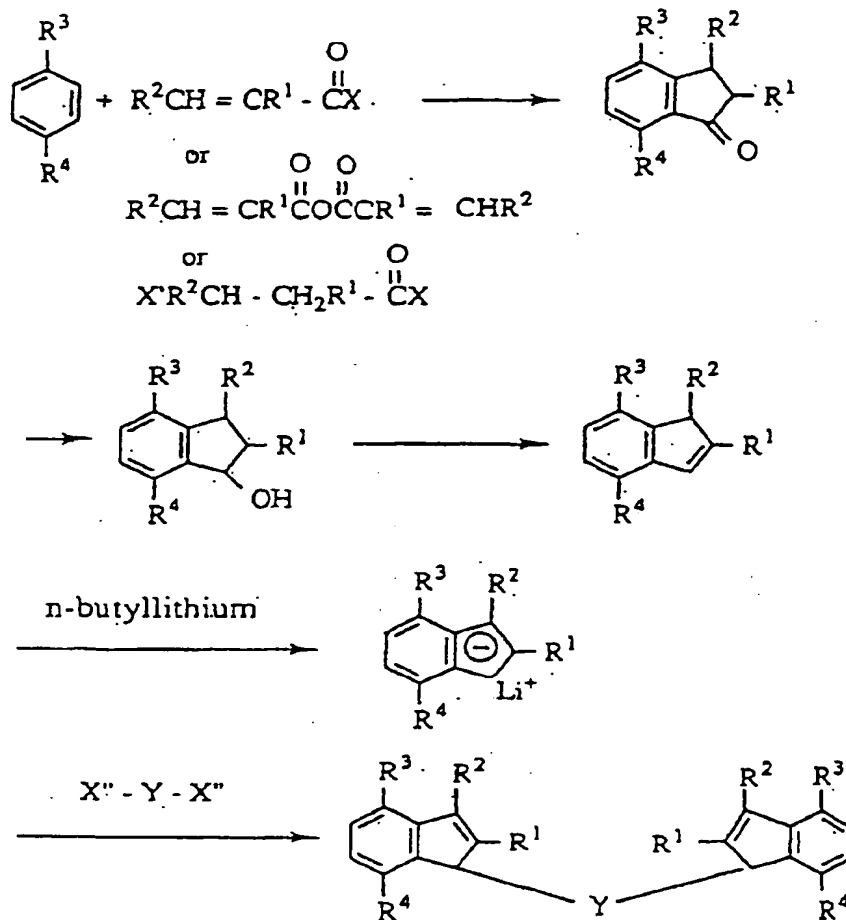
[0033] Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylarylsilylene group and an arylsilylene group.

[0034] Examples of the silicon-containing groups include methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methylphenylsilylene, diphenylsilylene, di(p-tolyl)silylene and di(p-chlorophenyl)silylene.

[0035] Listed below are examples of the transition metal compounds represented by the above formula (I).

rac-Dimethylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diethylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(i-propyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(n-butyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(cyclohexyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Methylphenylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diphenylsilyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-tolyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-chlorophenyl)silyl-bis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diethylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(i-propyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(n-butyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(cyclohexyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Methylphenylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Diphenylsilyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-tolyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Di(p-chlorophenyl)silyl-bis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium dimethyl,
 rac-Dimethylsilyl-bis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium methylchloride,
 rac-Dimethylsilyl-bis{1-(2-methyl-3-methyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-ethyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
 rac-Dimethylsilyl-bis{1-(2-phenyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,

[0036] The indene derivative ligand of the transition metal compound of the invention can be synthesized by an organic synthesis method conventionally used through the following reaction route.



(wherein each of X, X' and X'' is a halogen atom.)

[0037] The transition metal compound of the invention can be synthesized from the indene derivative by conventionally known methods, for example, by the method described in JP-A-268307/1993.

[0038] The transition metal compound of the invention can be used as an olefin polymerization catalyst component in combination with an organoaluminium oxy-compound.

[0039] The transition metal compound is usually used as an olefin polymerization catalyst component in the form of a racemic mixture, but the R configuration or the S configuration can be also used.

[0040] The olefin polymerization catalyst containing the above-mentioned transition metal compound as a catalyst component is now described.

[0041] The meaning of the term "polymerization" used herein is not limited to "homopolymerization" but may include "copolymerization". Also, the meaning of the term "polymer" used herein is not limited to "homopolymer" but may include "copolymer".

[0042] The first and second embodiments of olefin polymerization catalysts of the invention are now described.

[0043] The first olefin polymerization catalyst of the invention comprises:

(A) a transition metal compound of formula (I) (sometimes referred to as "component (A)" hereinafter); and

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

[0044] The second olefin polymerization catalyst of the invention comprises:

(A) a transition metal compound of formula (I);

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound to form an ion pair; and

(C) an organoaluminium compound.

[0045] The organoaluminium oxy-compound (B-1) (hereinafter sometimes referred to as "component (B-1)") used for the first and the second olefin polymerization catalysts of the invention may be a conventionally known aluminoxane or may be a benzene-insoluble organoaluminium oxy-compound as described in JP-A-78687/1990.

[0046] The conventionally known aluminoxane can be prepared, for example, by the following processes:

(1) A process comprising allowing an organoaluminium compound such as a trialkylaluminium to react with a suspension of a compound having adsorbed water or a salt containing water of crystallization, for example, the hydrate of magnesium chloride, copper sulfate, aluminium sulfate, nickel sulfate or cerous chloride, in a hydrocarbon solvent.

(2) A process comprising allowing water, ice or water vapor to directly react with an organoaluminium compound such as a trialkylaluminium in a solvent such as benzene, toluene, ethyl ether or tetrahydrofuran.

(3) A process comprising allowing an organotin oxide such as dimethyltin oxide or dibutyltin oxide to react with an organoaluminium compound such as a trialkylaluminium in a solvent such as decane, benzene or toluene.

[0047] The aluminoxane may contain a small amount of an organometallic component. Moreover, the solvent or the unreacted organoaluminium compound may be distilled off from the recovered solution of aluminoxane described above, and the resultant product may be dissolved again in a solvent.

[0048] Examples of the organoaluminium compounds used for preparing the aluminoxane include:

trialkylaluminiums, such as trimethylaluminium, triethylaluminium, tripropylaluminium, triisopropylaluminium, tri-n-butylaluminium, triisobutylaluminium, tri-sec-butylaluminium, tri-tert-butylaluminium, tri-pentylaluminium, trihexylaluminium, tri-octylaluminium and tridecylaluminium;

tricycloalkylaluminiums, such as tricyclohexylaluminium and tricyclooctylaluminium;

dialkylaluminium halides, such as dimethylaluminium chloride, diethylaluminium chloride, diethylaluminium bromide and diisobutylaluminium chloride;

dialkylaluminium hydrides, such as diethylaluminium hydride and diisobutylaluminium hydride;

dialkylaluminium alkoxides, such as dimethylaluminium methoxide and diethylaluminium ethoxide; and

dialkylaluminium aryloxides, such as diethylaluminium phenoxide.

[0049] Of the organoaluminium compounds, trialkylaluminium and tricycloalkylaluminium are particularly preferred.

[0050] Further, there may be also used, as the organoaluminium compound for preparing the aluminoxane, isoprenylaluminium of formula (II):



wherein x, y and z are each a positive number, and $z \geq 2x$.

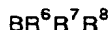
[0051] The organoaluminium compounds mentioned above may be used singly or in combination.

[0052] Solvents used for preparing the aluminoxane include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane and methylcyclopentane; petroleum fractions such as gasoline, kerosene and gas oil; and halides of the above-mentioned aromatic, aliphatic and alicyclic hydrocarbons, particularly chlorides and bromides thereof. In addition ethers such as ethyl ether and tetrahydrofuran may be also used. Of these solvents, particularly preferred are aromatic hydrocarbons.

[0053] Examples of the compounds which react with the transition metal compound (A) to form an ion pair (hereinafter sometimes referred to as "component (B-2)"), which are used for the first and the second olefin polymerization catalysts, include Lewis acids, ionic compounds, borane compounds and carborane compounds, as described in National Publications of International Patent No. 501950/1989 and No. 502036/1989, JP-A-179005/1992, JP-A-179006/1992, JP-A-207703/1992, JP-A-207704/1992, and US-A-547718.

[0054] The Lewis acid includes an Mg-containing Lewis acid, Al-containing Lewis acid and B-containing Lewis acid. Of these, a B-containing Lewis acid is preferred.

[0055] The Lewis acid containing a boron atom (B-containing Lewis acid) is, for example, a compound of formula:



wherein R^6 , R^7 and R^8 are each independently a phenyl group which may have a substituent such as a fluorine atom, a methyl group or a trifluoromethyl group, or a fluorine atom.

[0056] Examples of the compounds of the above formula include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron. Of these, tris(pentafluorophenyl)boron is particularly preferred.

[0057] The ionic compound used in the invention is a salt comprising a cationic compound and an anionic compound. An anion reacts with the transition metal compound (A) to make the transition metal compound (A) cationic and to form an ion pair so as to stabilize the transition metal cation seed. Examples of such anions include an organoboron compound anion, an organoarsenic compound anion, and an organoaluminium compound anion. Such anions are preferred as they are relatively bulky and stabilize the transition metal cation species. Examples of cations include a metallic cation, organometallic cation, carbonium cation, tripium cation, oxonium cation, sulfonium cation, phosphonium cation and ammonium cation. More specifically, there can be mentioned a triphenylcarbenium cation, tributylammonium cation, N,N-dimethylammonium cation and ferrocenium cation.

[0058] Of these, preferred are ionic compounds containing a boron compound as an anion. More specifically, examples of trialkyl-substituted ammonium salts include triethylammoniumtetra(phenyl)boron, tripropylammoniumtetra(phenyl)boron, tri(n-butyl)ammoniumtetra(phenyl)boron, trimethylammoniumtetra(p-tolyl)boron, trimethylammoniumtetra(o-tolyl)boron, tributylammoniumtetra(pentafluorophenyl)boron, tripropylammoniumtetra(o,p-dimethylphenyl)boron, tributylammoniumtetra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-trifluoromethylphenyl)boron, tri(n-butyl)ammoniumtetra(o-tolyl)boron and tri(n-butyl)ammoniumtetra(4-fluorophenyl)boron.

[0059] Examples of N,N-dialkylanilinium salts include N,N-dimethylaniliniumtetra(phenyl)boron, N,N-diethylaniliniumtetra(phenyl)boron and N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

[0060] Examples of dialkylammonium salts include di(n-propyl)ammoniumtetra(pentafluorophenyl)boron and dicyclohexylammoniumtetra(phenyl)boron.

[0061] Examples of triarylphosphonium salts include triphenylphosphoniumtetra(phenyl)boron, tri(methylphenyl)phosphoniumtetra(phenyl)boron and tri(dimethylphenyl)phosphoniumtetra(phenyl)boron.

[0062] Also employable as the ionic compound containing a boron atom are triphenylcarbeniumtetrakis-(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate and ferroceniumtetrakis(pentafluorophenyl)borate.

[0063] Further, the following compounds can be also employed. (In the ionic compounds enumerated below, the counter ion is tri(n-butyl)ammonium, but the counter ion is in no way limited thereto.)

[0064] That is, there can be mentioned salts of anions, for example, bis{tri(n-butyl)ammonium}nonaborate, bis{tri(n-butyl)ammonium}decaborate, bis{tri(n-butyl)ammonium}undecaborate, bis{tri(n-butyl)ammonium}dodecaborate, bis{tri(n-butyl)ammonium}decachlorododecaborate, bis{tri(n-butyl)ammonium}dodecachlorododecaborate, tri(n-butyl)ammonium-1-carbadecaborate, tri(n-butyl)ammonium-1-carbaundecaborate, tri(n-butyl)ammonium-1-carbadodecaborate, tri(n-butyl)ammonium-1-trimethylsilyl-1-carbadecaborate and tri(n-butyl)ammoniumbromo-1-carbadecaborate.

[0065] Moreover, borane compounds and carborane compounds can be also employed. These compounds are employed as the Lewis acid or the ionic compounds.

[0066] Examples of the borane compounds and the carborane compounds include:

borane and carborane complex compounds and salts of carborane anion, for example, decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydride-7,8-dimethyl-7,8-dicarbaundecaborane, dodecahydride-11-methyl-2,7-dicarbaundecaborane, tri(n-butyl)ammonium-6-carbadecaborate(14), tri(n-butyl)ammonium-6-carbadecaborate(12), tri(n-butyl)ammonium-7-carbaundecaborate(13), tri(n-butyl)ammonium-7,8-dicarbaundecaborate(12), tri(n-butyl)ammonium-2,9-dicarbaundecaborate(12), tri(n-butyl)ammoniumdodecahydride-8-methyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-ethyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-butyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-8-allyl-7,9-dicarbaundecaborate, tri(n-butyl)ammoniumundecahydride-9-trimethylsilyl-7,8-dicarbaundecaborate and tri(n-butyl)ammoniumundecahydride-4,6-dibromo-7-carbaundecaborate; and carborane and salts of carborane, for example, 4-carbanonaborane(14), 1,3-dicarbanonaborane(13), 6,9-dicarbadecaborane(14), dodecahydride-1-phenyl-1,3-dicarbanonaborane, dodecahydride-1-methyl-1,3-dicarbanonaborane and undecahydride-1,3-dimethyl-1,3-dicarbanonaborane.

[0067] Furthermore, the following compounds can be also employed. (In the ionic compounds enumerated below, the counter ion is tri(n-butyl)ammonium, but the counter ion is in no way limited thereto.)

[0068] That is, there can be mentioned salts of metallic carborane and metallic borane anion, for example, tri(n-butyl)ammoniumbis(nonahydride-1,3-dicarbononaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)nickelate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)cuprate(III), tri(n-butyl)ammoniumbis(undecahydride-7,8-dicarbaundecaborate)aurate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)ferrate(III), tri(n-butyl)ammoniumbis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborate)chromate(III), tri(n-butyl)ammoniumbis(tribromooctahydride-7,8-dicarbaundecaborate)cobaltate(III), tri(n-butyl)ammoniumbis(dodecahydride-dedicarbadodecaborate)-cobaltate(III), bis(tri(n-butyl)ammonium)bis(dodecahydride-dodecaborate)-nickelate(III), tris(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)chromate(III), bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)manganate(IV), bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)cobaltate(III) and bis(tri(n-butyl)ammonium)bis(undecahydride-7-carbaundecaborate)nickelate(IV).

[0069] The compounds (B-2) which react with the transition metal compound (A) to form an ion pair can be used in combination of two or more kinds.

[0070] The organoaluminium compound (C) (hereinafter sometimes referred to as "component (C)") used for the second olefin polymerization catalyst of the invention is, for example, an organoaluminum compound of formula (III):



wherein R^9 is a hydrocarbon group of 1 to 12 carbon atoms, X is a halogen atom or a hydrogen atom, and n is 1 to 3.

[0071] In formula (III), R^9 is, for example, an alkyl group, a cycloalkyl group or an aryl group. Particular examples include methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl.

[0072] Examples of such organoaluminium compounds (C) include:

trialkylaluminiums, such as trimethylaluminium, triethylaluminium, triisopropylaluminium, triisobutylaluminium, tri-octylaluminium and tri(2-ethylhexyl) aluminium;
alkenylaluminiums, such as isoprenylaluminium;
dialkylaluminium halides, such as dimethylaluminium chloride, diethylaluminium chloride, diisopropylaluminium chloride, diisobutylaluminium chloride and dimethylaluminium bromide;
alkylaluminium sesquihalides, such as methylaluminium sesquichloride, ethylaluminium sesquichloride, isopropylaluminium sesquichloride, butylaluminium sesquichloride and ethylaluminium sesquibromide;
alkylaluminium dihalides, such as methylaluminium dichloride, ethylaluminium dichloride, isopropylaluminium dichloride and ethylaluminium dibromide; and
alkylaluminium hydrides, such as diethylaluminium hydride and diisobutylaluminium hydride.

[0073] Also employable as the organoaluminium compound (C) is a compound of formula (IV):



wherein R^9 is the same hydrocarbon as in the above formula (III); L is an $-OR^{10}$ group, $-OSiR^{11}_3$ group, $-OAlR^{12}_2$ group, $-NR^{13}_2$ group, $-SiR^{14}_3$ group or $-N(R^{15})AlR^{16}_2$ group; n is 1 to 2; R^{10} , R^{11} , R^{12} and R^{16} are each, for example, methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl; R^{13} is, for example, hydrogen, methyl, ethyl, isopropyl, phenyl or trimethylsilyl; and R^{14} and R^{15} are each, for example, methyl or ethyl.

[0074] Examples of such organoaluminium compounds (C) include:

- (1) compounds of formula $R^9_n Al(OR^{10})_{3-n}$, for example, dimethylaluminium methoxide, diethylaluminium ethoxide and diisobutylaluminium methoxide;
- (2) compounds of formula $R^9_n Al(OSiR^{11}_3)_{3-n}$, for example, $Et_2Al(OSiMe_3)$, $(iso-Bu)_2Al(OSiMe_3)$ and $(iso-Bu)_2Al(OSiEt_3)$;
- (3) compounds of formula $R^9_n Al(OAlR^{12}_2)_{3-n}$, for example, $Et_2AlOAlEt_2$ and $(iso-Bu)_2AlOAl(iso-Bu)_2$;
- (4) compounds of formula $R^9_n Al(NR^{13}_2)_{3-n}$, for example, Me_2AlNEt_2 , $Et_2AlNHMe$, $Me_2AlNHet$, $Et_2AlN(SiMe_3)_2$ and $(iso-Bu)_2AlN(SiMe_3)_2$;
- (5) compounds of formula $R^9_n Al(SiR^{14}_3)_{3-n}$, for example, $(iso-Bu)_2AlSiMe_3$; and

(6) compounds of formula $R^9_nAl(N(R^{15})AlR^{16}_2)_{3-n}$, for example, $Et_2AlN(Me)AlEt_2$ and $(iso-Bu)_2AlN(Et)Al(iso-Bu)_2$.

[0075] Of the organoaluminium compounds of formulae (III) and (IV), the compounds of formulae R^9_3Al , $R^9_nAl(OR^{10})_{3-n}$ and $R^9_nAl(OAIR^{12}_2)_{3-n}$ are preferred, and the compounds having these formulae wherein R is an isoalkyl group and n is 2 are particularly preferred.

[0076] In the present invention, water may be used as a catalyst component in addition to component (A), component (B-1), component (B-2) and component (C). As the water employable in the invention, there can be mentioned water dissolved in a polymerization solvent described later, and adsorbed water or water of crystallization contained in a compound or a salt used for preparing component (B-1).

[0077] The first olefin polymerization catalyst of the invention can be prepared by mixing component (A) and component (B-1) (or component (B-2)), and if desired water (as a catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent).

[0078] There is no specific limitation on the order of mixing those components, but it is preferred that component (B-1) (or component (B-2)) is mixed with water, followed by mixing with component (A).

[0079] The second olefin polymerization catalyst of the invention can be prepared by mixing component (A), component (B-1) (or component (B-2)) and component (C), and if desired water (as a catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent).

[0080] There is no specific limitation on the order of mixing those components. However, when component (B-1) is used, it is preferred that component (B-1) is mixed with component (C), followed by mixing with component (A). When component (B-2) is used, it is preferred that component (C) is mixed with component (A), followed by mixing with component (B-2).

[0081] In the mixing of each component, the atomic ratio (Al:transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 10,000:1, preferably 20:1 to 5,000:1; and the concentration of component (A) is 10^{-8} to 10^{-1} mol/liter-medium, preferably 10^{-7} to 5×10^{-2} mol/liter-medium.

[0082] When component (B-2) is used, the molar ratio (component (A):component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1, and the concentration of component (A) is 10^{-8} to 10^{-1} mol/liter-medium, preferably 10^{-7} to 5×10^{-2} mol/liter-medium.

[0083] In the preparation of the second olefin polymerization catalyst of the invention, the atomic ratio ($Al_C:Al_{B-1}$) of the aluminum atoms (Al_C) in component (C) to the aluminum atoms (Al_{B-1}) in component (B-1) is usually 0.02:1 to 20:1, preferably 0.2:1 to 10:1.

[0084] When water is used as a catalyst component, the molar ratio ($Al_{B-1}:H_2O$) of the aluminum atoms (Al_{B-1}) in component (B-1) to water (H_2O) is 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0085] The above-mentioned components may each be mixed in a polymerizer, or a mixture of those components beforehand prepared may be fed to a polymerizer.

[0086] If the components are beforehand mixed, the mixing temperature is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0087] Examples of the media (solvents) used for preparing the olefin polymerization catalyst according to the invention includes:

aliphatic hydrocarbons, such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane and kerosene;

alicyclic hydrocarbons, such as cyclopentane, cyclohexane and methylcyclopentane;

aromatic hydrocarbons, such as benzene, toluene and xylene;

halogenated hydrocarbons, such as ethylene chloride, chlorobenzene and dichloromethane; and mixtures of these hydrocarbons.

[0088] Next, the third and fourth embodiments of olefin polymerization catalysts of the invention are described.

[0089] The third olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I); and

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair;

said transition metal compound (A) and said at least one compound (B) being supported on the fine particle carrier.

[0090] The fourth olefin polymerization catalyst of the invention comprises:

a solid catalyst component comprising:

a fine particle carrier,

(A) a transition metal compound of formula (I), and
(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair,

said transition metal compound (A) and said at least one compound (B) being supported on the fine particle carrier; and

(C) an organoaluminium compound.

[0091] The transition metal compound (A) used for the third and fourth olefin polymerization catalysts of the invention is the same as that for the aforesaid first and second olefin polymerization catalysts, and is represented by the above formula (I).

[0092] Examples of the organoaluminium oxy-compounds (B-1) used for the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0093] Examples of the compounds (B-2) which react with the transition metal compound (A) to form an ion pair and used for the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0094] Examples of the organoaluminium compounds (C) used for the fourth olefin polymerization catalyst of the invention are the same as those used for the second olefin polymerization catalyst.

[0095] The fine particle carrier used for the third and fourth olefin polymerization catalysts of the invention is an inorganic or organic compound, and is a particulate or granular solid having a particle diameter of 10 to 300 μm , preferably 20 to 200 μm .

[0096] The inorganic carrier is preferably a porous oxide, and examples include SiO_2 , Al_2O_3 , MgO , ZrO_2 , TiO_2 , B_2O_3 , CaO , ZnO , BaO , ThO_2 , and mixtures thereof such as $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr}_2\text{O}_3$ and $\text{SiO}_2\text{-TiO}_2\text{-MgO}$. Of these, preferred is a carrier containing SiO_2 and/or Al_2O_3 as its major component.

[0097] The above-mentioned inorganic oxides may contain carbonates, sulfates, nitrates and oxides, such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O and Li_2O , in a small amount.

[0098] The properties of the fine particle carrier vary depending on the kind and process for the preparation thereof, but a preferred carrier has a specific surface area of 50 to 1,000 m^2/g , preferably 100 to 700 m^2/g , and a pore volume of 0.3 to 2.5 cm^3/g . The fine particle carrier is used after being calcined, if necessary, at 100 to 1,000 $^\circ\text{C}$, preferably 150 to 700 $^\circ\text{C}$.

[0099] Also employable as the fine particle carrier in the invention is a granular or particulate solid of an organic compound having a particle diameter of 10 to 300 μm .

Examples of the organic compounds include (co)polymers prepared mainly from α -olefins of 2 to 14 carbon atoms such as ethylene, propylene, 1-butene and 4-methyl-1-pentene, and (co)polymers prepared mainly from vinylcyclohexane or styrene.

[0100] The fine particle carrier may contain surface hydroxyl groups or water. In this case, the surface hydroxyl groups are contained in an amount of not less than 1.0 % by weight, preferably 1.5 to 4.0 % by weight, more preferably 2.0 to 3.5 % by weight; and water is contained in an amount of not less than 1.0 % by weight, preferably 1.2 to 20 % by weight, more preferably 1.4 to 15 % by weight. The water contained in the fine particle carrier means water which is adsorbed on the surface of the fine particle carrier.

[0101] The amount (% by weight) of the adsorbed water and the amount (% by weight) of the surface hydroxyl group in the fine particle carrier can be determined in the following manner.

Amount of adsorbed water

[0102] The weight reduction of the fine particle carrier after drying at 200 $^\circ\text{C}$ under ordinary pressure for 4 hours in

a stream of nitrogen is measured, and the percentage of the weight after the drying to the weight before the drying is calculated.

Amount of surface hydroxyl groups

[0103] The weight of the fine particle carrier after drying at 200 °C under ordinary pressure for 4 hours in a stream of nitrogen is taken as X (g). The carrier is calcined at 1,000 °C for 20 hours to obtain a calcined product containing no surface hydroxyl groups. The weight of the calcined product thus obtained is taken as Y (g). The amount (% by weight) of the surface hydroxyl groups is calculated from the following formula.

$$\text{Amount (wt.\%) of surface hydroxyl groups} = \{(X-Y)/X\} \times 100$$

[0104] If a fine particle carrier having a specific amount of adsorbed water or a specific amount of surface hydroxyl groups as described above is used, an olefin polymerization catalyst capable of preparing an olefin polymer having excellent particle properties and having a high polymerization activity can be obtained.

[0105] Further, in the third and the fourth olefin polymerization catalysts of the invention, water as described in the first and second olefin polymerization catalysts may be used as a catalyst component.

[0106] The third olefin polymerization catalyst of the invention (i.e., solid catalyst component) can be prepared by mixing the fine particle carrier, component (A) and component (B-1) (or component (B-2)), and, if desired, water (catalyst component), in an inert hydrocarbon medium (solvent) or an olefin medium (solvent). In the mixing of those components, component (C) can be further added.

[0107] There is no specific limitation on the order of mixing those components.

[0108] However, preferred processes are:

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2), and then with component (A), followed by mixing with water if desired;

a process in which a mixture of component (B-1) (or component (B-2)) and component (A) is mixed and contacted with the fine particle carrier, followed by mixing with water if desired; and

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)) and water, followed by mixing with component (A).

[0109] In the mixing of each components, component (A) is usually used in an amount of 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, per 1 g of the fine particle carrier; and the concentration of component (A) is generally 5×10^{-6} to 2×10^{-2} mol/liter-medium, preferably 2×10^{-5} to 10^{-2} mol/liter-medium. The atomic ratio (Al: transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 3,000:1; preferably 20:1 to 2,000:1. When component (B-2) is used, the molar ratio (component (A): component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1.

[0110] When water is used as a catalyst component, the molar ratio ($\text{Al}_{\text{B-1}}:\text{H}_2\text{O}$) of the aluminium atoms ($\text{Al}_{\text{B-1}}$) in component (B-1) to water (H_2O) is range of 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0111] The temperature for mixing the components is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0112] The fourth olefin polymerization catalyst of the invention is formed from the above-mentioned third olefin polymerization catalyst (solid catalyst component) and the organoaluminium compound (C). Component (C) is used in an amount of not more than 500 mol, preferably 5 to 200 mol, per 1 g of the transition metal atoms in component (A) contained in the solid catalyst component.

[0113] The third and the fourth olefin polymerization catalysts of the invention may contain other components useful for olefin polymerization.

[0114] Examples of the inert hydrocarbon media (solvents) used for preparing the third and the fourth olefin polymerization catalysts of the invention are the same as those used for the first and the second olefin polymerization catalysts.

[0115] Next, the fifth and the sixth embodiments of olefin polymerization catalysts of the invention are described.

[0116] The fifth olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I);

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair; and

a prepolymerized olefin polymer produced by prepolymerization.

[0117] The sixth olefin polymerization catalyst of the invention comprises:

a fine particle carrier;

(A) a transition metal compound of formula (I);

(B) at least one compound selected from

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair;

(C) an organoaluminium compound; and

a prepolymerized olefin polymer produced by prepolymerization.

[0118] Examples of the fine particle carrier used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those for the third and fourth olefin polymerization catalysts.

[0119] The transition metal compound (A) used for the fifth and sixth olefin polymerization catalysts of the invention is the same as that for the first and second olefin polymerization catalysts, and is represented by formula (I).

[0120] Examples of the organoaluminium oxy-compounds (B-1) used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for the first and second olefin polymerization catalysts.

[0121] Examples of the compounds (B-2) which react with the transition metal compound (A) to form an ion pair and used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for the first and second olefin polymerization catalysts.

[0122] Examples of the organoaluminium compounds (C) used for the sixth olefin polymerization catalyst of the invention are the same as those used for the second olefin polymerization catalyst.

[0123] Further, in the fifth and sixth olefin polymerization catalysts of the invention, water as described in the first and second olefin polymerization catalysts may be used as a catalyst component.

[0124] The fifth olefin polymerization catalyst of the invention can be prepared by prepolymerizing a small amount of an olefin to the solid catalyst component. The solid catalyst component is obtained by mixing the fine particle carrier, component (A) and component (B-1) (or component (B-2)), and if desired water, in an inert hydrocarbon medium (solvent) or an olefin medium (solvent). In the mixing of those components, component (C) can be further added.

[0125] There is no specific limitation on the order of mixing those components.

[0126] However, preferred processes are:

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)), and then with component (A), followed by mixing with water if desired

a process in which a mixture of component (B-1) (or component (B-2)) and component (A) is mixed and contacted with the fine particle carrier, followed by mixing with water if desired; and

a process in which the fine particle carrier is mixed and contacted with component (B-1) (or component (B-2)) and water, followed by mixing with component (A).

[0127] The mixing of the components is desirably carried out with stirring.

[0128] In the mixing of each component, component (A) is usually used in an amount of 10^{-6} to 5×10^{-3} mol, preferably 3×10^{-6} to 10^{-3} mol, per 1 g of the fine particle carrier; and the concentration of component (A) is generally 5×10^{-6} to 2×10^{-2} mol/liter-medium, preferably 10^{-5} to 10^{-2} mol/liter-medium. The atomic ratio (Al:transition metal) of aluminium in component (B-1) to the transition metal in component (A) is usually 10:1 to 3,000:1, preferably 20:1 to 2,000:1. When component (B-2) is used, the molar ratio (component (A):component (B-2)) of component (A) to component (B-2) is usually 0.01:1 to 10:1, preferably 0.1:1 to 5:1.

[0129] When water is used as a catalyst component, the molar ratio ($Al_{B-1}:H_2O$) of aluminium atoms (Al_{B-1}) in component (B-1) to water (H_2O) is 0.5:1 to 50:1, preferably 1:1 to 40:1.

[0130] The temperature for mixing the components is usually -50 to 150 °C, preferably -20 to 120 °C; and the contact

time is 1 to 1,000 minutes, preferably 5 to 600 minutes. The mixing temperature may be varied while the components are mixed and contacted with each other.

[0131] The fifth olefin polymerization catalyst of the invention can be prepared by prepolymerizing an olefin in the presence of the above-mentioned components. The prepolymerization can be carried out by introducing an olefin into an inert hydrocarbon medium (solvent) in the presence of the components and, if necessary, component (C).

[0132] In the prepolymerization, component (A) is usually used in an amount of 10^{-5} to 2×10^{-2} mol/liter, preferably 5×10^{-5} to 10^{-2} mol/liter. The prepolymerization temperature is -20 to 80 °C, preferably 0 to 50 °C; and the prepolymerization time is 0.5 to 100 hours, preferably about 1 to 50 hours.

[0133] The olefin used for the prepolymerization is selected from olefins which are used for polymerization. It is preferable to use the same monomer as used in the polymerization or a mixture of the same monomer as used in the polymerization and an α -olefin.

[0134] In the olefin polymerization catalyst of the invention obtained as above, it is desired that the transition metal atoms are supported in an amount of 10^{-6} to 10^{-3} g-atom, preferably 2×10^{-6} to 3×10^{-4} g-atom, per 1 g of the fine particle carrier; and the aluminium atom are supported in an amount of 10^{-3} to 10^{-1} g-atom, preferably 2×10^{-3} to 5×10^{-2} g-atom, per 1 g of the fine particle carrier. Further, it is also desired that component (B-2) is supported in an amount of 5×10^{-7} to 0.1 g-atom, preferably 2×10^{-7} to 3×10^{-2} g-atom, in terms of the boron atoms contained in component (B-2).

[0135] The amount of prepolymerized polymer prepared by the prepolymerization is desirably 0.1 to 500 g, preferably 0.3 to 300 g, particularly preferably 1 to 100 g, per 1 g of the fine particle carrier.

[0136] The sixth olefin polymerization catalyst of the invention is formed from the fifth olefin polymerization catalyst (component) and the organoaluminium compound (C). The organoaluminium compound (C) is used in an amount of not more than 500 mol, preferably 5 to 200 mol, per 1 g-atom of the transition metal atoms in the component (A).

[0137] The fifth and sixth olefin polymerization catalysts of the invention may contain other components useful for the olefin polymerization.

[0138] Examples of the inert hydrocarbon solvents used for the fifth and sixth olefin polymerization catalysts of the invention are the same as those used for preparing the first and second olefin polymerization catalysts.

[0139] Polyolefins obtained by the use of the olefin polymerization catalysts as described above have a narrow molecular weight distribution, a narrow composition distribution and a high molecular weight and the olefin polymerization catalysts have a high polymerization activity.

[0140] Further, when olefins of 3 or more carbon atoms are polymerized in the presence of the olefin polymerization catalysts, polyolefins having excellent stereoregularity can be obtained.

[0141] Next, the process for olefin polymerization according to the present invention is described.

[0142] An olefin is polymerized in the presence of any of the above-described olefin polymerization catalysts. The polymerization may be carried out by a liquid phase polymerization process such as suspension polymerization or by a gas phase polymerization.

[0143] In the liquid phase polymerization process, the same inert hydrocarbon solvent as used in the preparation of the catalyst can be used, or the olefin itself can be also used as a solvent.

[0144] In the polymerization of an olefin using the first or second polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system.

[0145] In the polymerization of an olefin using the third or fourth polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system. In this case, an aluminosilicate which is not supported on the carrier may be employed, if desired.

[0146] In the polymerization of an olefin using the fifth or sixth polymerization catalyst, the catalyst is usually used in an amount of 10^{-8} to 10^{-3} g-atom/liter, preferably 10^{-7} to 10^{-4} g-atom/liter, in terms of concentration of the transition metal atoms of component (A) in the polymerization system. In this case, an aluminosilicate which is not supported on the carrier may be employed, if desired.

[0147] In the slurry polymerization, the temperature for the olefin polymerization is usually -50 to 100 °C, preferably 0 to 90 °C. In the liquid phase polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization process, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The polymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the polymerization may be performed in two or more stages having different reaction conditions.

[0148] The molecular weight of the resulting olefin polymer can be regulated by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature.

[0149] Examples of the olefins to be polymerized using the olefin polymerization catalysts of the invention include:

α -olefins of 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; and cycloolefins of 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene.

[0150] Also employable are styrene, vinylcyclohexane or diene.

[0151] When the olefin polymerization catalyst of the invention is used to polymerize an α -olefin of 3 or more carbon atoms, a polymer having a lower melting point is obtainable as compared with a polymer obtained by using a conventional metallocene type catalyst, even though the polymers have the almost the same molecular weight. Further, when the catalyst of the invention is used, a copolymer having a low melting point can be obtained even if the amount of recurring units derived from a comonomer is small.

[0152] If an α -olefin of 3 or more carbon atoms is polymerized using the olefin polymerization catalyst of the invention, a large number of inversely inserted monomer units are present in the molecules of the resultant olefin polymer. It is known that in the α -olefin prepared by a polymerization of an α -olefin of 3 or more carbon atoms in the presence of a chiral metallocene catalyst, 2,1-insertion or 1,3-insertion takes place in addition to the ordinary 1,2-insertion, whereby an inversely inserted unit such as a 2,1-insertion or 1,3-insertion is formed in the olefin polymer molecule (see: Makromol. Chem., Rapid Commun., 8,305 (1987), by K. Soga, T. Shiono, S. Takemura and W. Kaminsky). It is also known that when inverse insertions are present in the olefin polymer molecule, the melting point of the olefin polymer becomes low for its stereoregularity (see: Polymer, 30, 1350 (1989), by T. Tsutsui, N. Ishimura, A. Mizuno, A. Toyota and N. Kashiwa).

[0153] In the molecule of the olefin polymer obtained by polymerizing an α -olefin of 3 or more carbon atoms using the olefin polymerization catalyst of the invention, a large number of inversely inserted monomer units are present, and hence it is presumed that the melting point of the olefin polymer is lower than the melting point of an olefin polymer having almost the same molecular weight which is obtained by the use of a conventional catalyst.

[0154] The catalyst of the present invention may be used to prepare a propylene polymer, propylene copolymer or propylene elastomer.

Propylene polymer

[0155] The propylene polymer comprises propylene units, but may also contain constituent units derived from other olefins in an amount of less than 0.5 % by mol, preferably less than 0.3 % by mol, more preferably less than 0.1 % by mol.

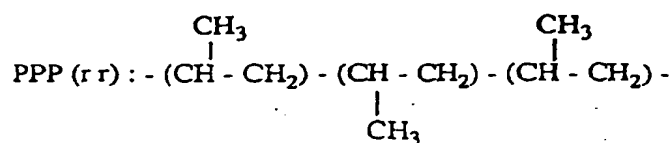
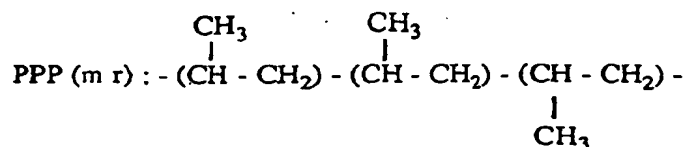
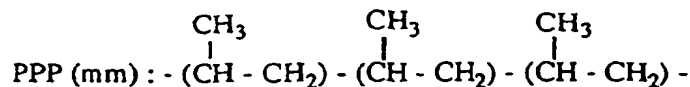
[0156] The propylene polymer has a triad tacticity of not less than 90 %, preferably not less than 93 %, more preferably not less than 95 %. The term "triad tacticity" means a proportion of chains of three propylene units (i.e., chains consisting of three propylene units continuously bonded) that the directions of methyl branches in the propylene chain are the same as each other and each propylene unit is bonded to each other with head-to-tail bonds, to total three propylene units-chains in the polymers. This term is sometimes referred to as "mm fraction" hereinafter.

[0157] The triad tacticity can be determined from a ^{13}C -NMR spectrum of the propylene polymer.

[0158] The ^{13}C -NMR spectrum is measured in the following manner. A 50 to 60 mg sample is completely dissolved in a mixed solvent containing about 0.5 ml of hexachlorobutadiene, o-dichlorobenzene or 1,2,4-trichlorobenzene and about 0.05 ml of deuterated benzene (i.e., lock solvent) in a NMR sample tube (diameter: 5 mm), and then subjected to a proton perfect decoupling method at 120 °C to measure the ^{13}C -NMR spectrum. The measurement is conducted under the conditions of a flip angle of 45° and a pulse interval of not less than 3.4 T_1 (T_1 is the maximum value with respect to the spin-lattice relaxation time of the methyl group). T_1 of the methylene group and T_1 of the methine group are each shorter than that of the methyl group, and hence the magnetization recovery of all carbons under these conditions is not less than 99 %.

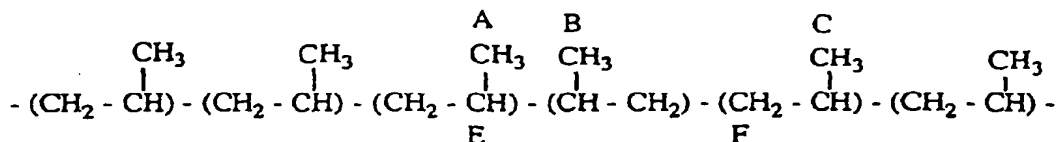
[0159] With respect to the chemical shift, the methyl group of the third unit in the 5 propylene units-chain consisting of head-to-tail bonds and having the same directions of the methyl branches is set to 21.593 ppm, and the chemical shifts of other carbon peaks are determined using the above-mentioned value as a reference. Accordingly, a peak based on the methyl group of the second unit in the three propylene units-chain having a PPP(mm) structure appears in the range of 21.1 to 21.8 ppm; a peak based on the methyl group of the second unit in the three propylene units-chain having a PPP(mr) structure appears in the range of 20.2 to 21.1 ppm; and a peak based on the methyl group of the second unit in the three propylene units-chain having PPP(rr) structure appears in the range of 19.4 to 20.2 ppm.

[0160] PPP(mm), PPP(mr) and PPP(rr) structures have the following 3 propylene units-chain structure with head-to-tail bonds, respectively.

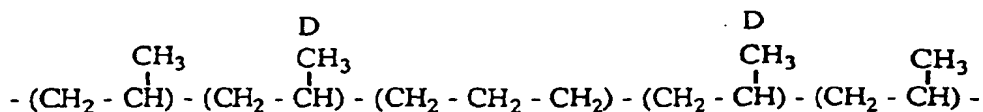


[0161] In addition to the ordered structures represented by PPP(mm), PPP(mr) and PPP(rr), the propylene polymer has a structure (i) containing an inversely inserted unit based on the 2,1-insertion and a structure (ii) containing an inversely inserted unit based on the 1,3-insertion, in small amounts.

Structure (i)



Structure (ii)



[0162] The aforementioned definition of the mm fraction is not applied to the propylene units having the carbons attached with marks A, B, C and D among the carbons attached with marks A to F. The carbon A and the carbon B resonate in the region of 16.5 to 17.5 ppm, the carbon C resonates in the vicinity of 20.8 ppm (mr region), and the carbon D resonates in the vicinity of 20.7 ppm (mr region). In the structure (i) and the structure (ii), however, not only the peak of the methyl group but also the peaks of the adjacent methylene and methine groups must be confirmed.

[0163] In the structure (ii), a $-(\text{CH}_2)_3-$ unit is produced and a unit corresponding to one methyl group disappears as a result of hydrogen transfer polymerization.

[0164] Accordingly, the mm fraction in all of the polymer chains can be represented by the following formula:

$$\text{mm Fraction (\%)} = \frac{\text{area of methyl group (21.1 ~ 21.8 ppm)}}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100$$

5 wherein ΣI_{CH_3} denotes the total areas of all peaks derived from the methyl groups.

[0165] Further, $I_{\alpha\delta}$ and $I_{\beta\gamma}$ are an area of $\alpha\delta$ peak (resonance in the vicinity of 37.1 ppm) and an area of $\beta\gamma$ peak (resonance in the vicinity 27.3 ppm), respectively. Naming of these methylene peaks was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781).

10 [0166] In the polymerization to prepare a propylene polymer, the 1,2-insertion of the propylene monomer mainly takes place, but the 2,1-insertion or the 1,3-insertion thereof sometimes takes place. The 2,1-insertion forms the inversely inserted unit represented by structure (i) in the polymer chain. The proportion of the 2,1-propylene monomer insertions to all propylene insertions was calculated by the following formula.

$$15 \quad \text{Proportion of inversely inserted units based on 2,1-insertion (\%)} = \frac{0.5 \times \{\text{area of methyl group (16.5 ~ 17.5 ppm)}\}}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100$$

[0167] Likewise, the proportion of the 1,3-propylene monomer insertions represented by structure (ii) to all propylene insertions was calculated by the following formula.

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$$\begin{aligned} &\text{Proportion of inversely} \\ &\text{inserted units based} = \frac{(I_{\alpha\delta} + I_{\beta\gamma}) / 4}{\Sigma I_{\text{CH}_3} + (I_{\alpha\delta} + I_{\beta\gamma}) / 4} \times 100 \\ 25 \quad &\text{on 3,1-insertion (\%)} \end{aligned}$$

The proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ^{13}C -NMR, is not less than 0.7 %, preferably 0.7 to 2.0 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion in all propylene insertions is not more than 0.05 %, preferably not more than 0.04 %, more preferably not more than 0.03 %.

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[0168] The propylene polymer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dl/g, preferably 0.5 to 12 dl/g, more preferably 1 to 12 dl/g.

35

[0169] The propylene polymer is prepared by polymerizing propylene in the presence of the aforesaid olefin polymerization catalysts. The polymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization and a solution polymerization) or a gas phase polymerization.

[0170] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, or propylene can be also used as a solvent.

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[0171] In the suspension polymerization, the temperature for polymerizing propylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The polymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The polymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the polymerization can be carried out in two or more stages having different reaction conditions.

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[0172] The molecular weight of the resultant propylene polymer can be regulated by allowing hydrogen to exist in the polymerization system or by varying the polymerization temperature and the polymerization pressure.

Propylene copolymer

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[0173] The propylene copolymer is a propylene/ethylene random copolymer containing propylene units in an amount of 95 to 99.5 % by mol, preferably 95 to 99 % by mol, more preferably 95 to 98 % by mol, and ethylene units in an amount of 0.5 to 5 % by mol, preferably 1 to 5 % by mol, more preferably 2 to 5 % by mol.

[0174] The propylene copolymer may contain constituent units derived from other olefins in an amount of not more than 5 % by mol.

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[0175] In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds, as measured by ^{13}C -NMR, is not less than 90 %, preferably not less than 93 %, more preferably not less than 96 %.

[0176] The triad tacticity (mm fraction) of the propylene copolymer can be determined from a ^{13}C -NMR spectrum of the propylene copolymer and the following formula:

$$\text{mm Fraction} = \frac{\text{PPP(mm)}}{\text{PPP(mm)} + \text{PPP(mr)} + \text{PPP(rr)}}$$

wherein PPP(mm); PPP(mr) and PPP(rr) denote the peak areas derived from the methyl groups of the second units in the three propylene units-chains consisting of head-to-tail bonds as defined above.

[0177] The ^{13}C -NMR spectrum of the propylene copolymer can be measured in the same manner as described for the propylene polymer. The spectrum relating to the methyl carbon region (16 - 23 ppm) can be classified into the first region (21.1 - 21.9 ppm), the second region (20.3 - 21.0 ppm), the third region (19.5 - 20.3 ppm) and the fourth region (16.5 - 17.5 ppm). Each peak in the spectrum was assigned with reference to "Polymer", 30 (1989) 1350.

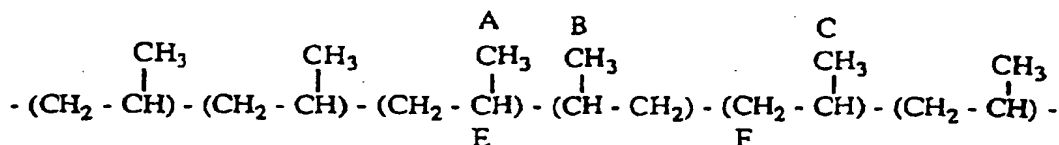
[0178] In the first region, the methyl group of the second unit in the three propylene units-chain represented by PPP (mm) resonates.

[0179] In the second region, the methyl group of the second unit in the three propylene units-chain represented by PPP(mr) resonates and the methyl group (PPE-methyl group) of a propylene unit whose adjacent units are a propylene unit and an ethylene unit resonates (in the vicinity of 20.7 ppm).

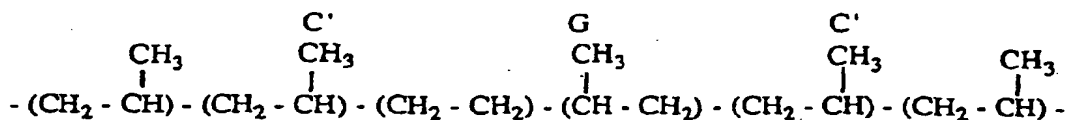
[0180] In the third region, the methyl group of the second unit in the three propylene units-chain represented by PPP (rr) resonates and the methyl group (EPE-methyl group) of a propylene unit whose adjacent units are ethylene units resonate (in the vicinity of 19.8 ppm).

[0181] Further, the propylene copolymer has the following structures (i) and (iii) containing an inversely inserted unit.

Structure (i)



Structure (iii)



[0182] Of the carbons attached with marks A to G, a peak of the carbon C and a peak of the carbon C' appear in the second region, a peak of the carbon G appears in the third region, and a peak of the carbon A and a peak of the carbon B appear in the fourth region.

[0183] Of the peaks which appear in the first to fourth regions as described above, peaks which are not based on the three propylene units-chain consisting of head-to-tail bonds are peaks based on the PPE-methyl group, the EPE-methyl group, the carbon C, the carbon C', the carbon G, the carbon A and the carbon B.

[0184] The peak area based on the PPE-methyl group can be evaluated by the peak area of the PPE-methine group (resonance in the vicinity of 30.6 ppm), and the peak area based on the EPE-methyl group can be evaluated by the peak area of the EPE-methine group (resonance in the vicinity of 32.9 ppm). The peak area based on the carbon C can be evaluated by 1/2 as much as the sum of the peak areas of the carbon F and the carbon E both having the inversely inserted structure (structure (i)) (resonance in the vicinity of 35.6 ppm and resonance in the vicinity of 35.4 ppm, respectively). The peak area based on the carbon C' can be evaluated by 1/2 as much as the sum of the peak areas of the $\alpha\beta$ methylene carbons having the inversely inserted structure (structure (iii)) (resonance in the vicinity of 34.3 ppm and resonance in the vicinity of 34.5 ppm, respectively). The peak area based on the carbon G can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.7 ppm).

[0185] Accordingly, by subtracting these peak areas from the total peak areas of the second region and the third region, the peak areas based on the three propylene units-chains (PPP(mr) and PPP(rr)) consisting of head-to-tail bonds can be obtained.

[0186] Since the positions of the carbon A peak and the carbon B peak have no concern with the peak of the three

propylene units-chain (PPP), they do not need to be taken into account.

[0187] Thus, the peak areas of PPP(mm), PPP(mr) and PPP(rr) can be evaluated, and hence the triad tacticity of the propylene unit chain consisting of head-to tail bonds can be determined.

[0188] In the propylene copolymer, the proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ^{13}C -NMR, is not less than 0.5 %, preferably 0.5 to 1.5 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer in all propylene insertions is not more than 0.05 %, preferably not more than 0.04 %, more preferably not more than 0.03 %.

[0189] In the polymerization, the 1,2-insertion of the propylene monomer (i.e., the methylene side is bonded to the catalyst) mainly takes place, but the 2,1-insertion thereof sometimes takes place. The 2,1-insertion forms the inversely inserted unit in the polymer.

[0190] The proportion of the 2,1-insertions to all propylene insertions in the propylene copolymer was calculated by the following formula with reference to "Polymer", 30 (1989) 1350.

Proportion of inversely inserted unit based on 2,1-insertion (%)

$$= \frac{0.5 I_{\alpha\beta} (\text{structure (i)}) + 0.25 I_{\alpha\beta} (\text{structure (iii)})}{I_{\alpha\gamma} + I_{\alpha\beta} (\text{structure (i)}) + 0.5 (I_{\alpha\gamma} + I_{\alpha\beta} (\text{structure (iii)}) + I_{\alpha\delta})} \times 100$$

[0191] Naming of the peaks in the above formula was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781). $I_{\alpha\delta}$ denotes a peak area of the $\alpha\delta$ peak.

[0192] The proportion (%) of the amount of the three propylene units-chains based on the 1,3-insertion was determined by dividing 1/2 as much as the area of the $\beta\gamma$ peak (resonance in the vicinity of 27.4 ppm) by the sum of all the methyl group peaks and 1/2 as much as the $\beta\gamma$ peak, and then multiplying the resulting value by 100.

[0193] The propylene copolymer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dl/g, preferably 0.5 to 12 dl/g, more preferably 1 to 12 dl/g.

[0194] The propylene copolymer is prepared by copolymerizing propylene and ethylene in the presence of the aforesaid olefin polymerization catalysts. The copolymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization and a solution polymerization) or a gas phase polymerization.

[0195] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, and propylene and/or ethylene can be also used as a solvent.

[0196] In the suspension polymerization, the temperature for copolymerizing propylene and ethylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The copolymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The copolymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the copolymerization can be carried out in two or more stages having different reaction conditions.

[0197] The molecular weight of the resultant propylene copolymer can be regulated by allowing hydrogen to exist in the copolymerization system or by varying the copolymerization temperature and the copolymerization pressure.

Propylene elastomer

[0198] The propylene elastomer is a propylene/ethylene random copolymer containing propylene units in an amount of 50 to 95 % by mol, preferably 60 to 93 % by mol, more preferably 70 to 90 % by mol, and containing ethylene units in an amount of 5 to 50 % by mol, preferably 7 to 40 % by mol, more preferably 10 to 30 % by mol.

[0199] The propylene elastomer may contain constituent units derived from other olefins in an amount of not more than 10 % by mol.

[0200] In the propylene elastomer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds, as measured by ^{13}C -NMR, is not less than 90.0 %, preferably not less than 92.0 %, more preferably not less than 95.0 %.

[0201] The triad tacticity (mm fraction) of the propylene elastomer can be determined from a ^{13}C -NMR spectrum of the propylene elastomer and the following formula:

$$\text{mm Fraction} = \frac{\text{PPP(mm)}}{\text{PPP(mm)} + \text{PPP(mr)} + \text{PPP(rr)}}$$

wherein PPP(mm), PPP(mr) and PPP(rr) have the same meanings as above.

[0202] The ^{13}C -NMR spectrum of the propylene elastomer can be measured in the same manner as described for the propylene polymer. The spectrum relating to the methyl carbon region (19 - 23 ppm) can be classified into the first region (21.2 - 21.9 ppm), the second region (20.3 - 21.0 ppm) and the third region (19.5 - 20.3 ppm). Each peak in the

spectrum was assigned with reference to a literature "Polymer", 30 (1989) 1350.

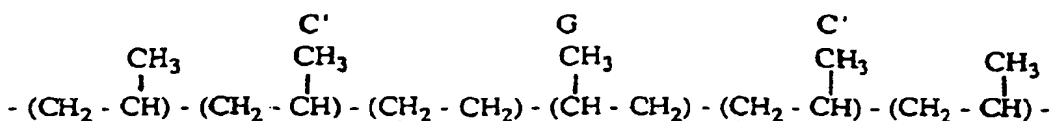
[0203] In the first region, the methyl group of the second unit in the three propylene units-chain represented by PPP (mm) resonates.

[0204] In the second region, the methyl group of the second unit in the three propylene units-chain represented by PPP(mr) resonates and the methyl group (PPE-methyl group) of a propylene unit whose adjacent units are a propylene unit and an ethylene unit resonates (in the vicinity of 20.7 ppm).

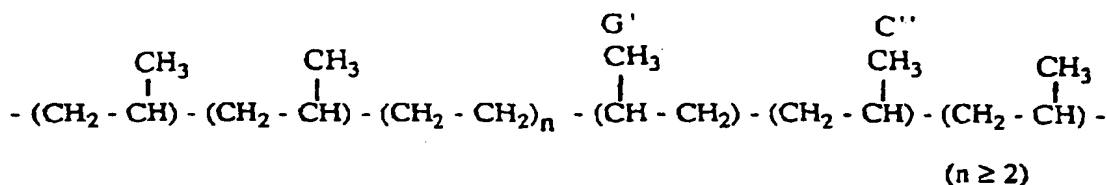
[0205] In the third region, the methyl group of the second unit in the three propylene units-chain represented by PPP (rr) resonates and the methyl group (EPE-methyl group) of a propylene unit whose adjacent units are ethylene units resonates (in the vicinity of 19.8 ppm).

[0206] Further, the propylene elastomer has the following structures (iii) and (iv) containing an inversely inserted unit.

Structure (iii)



Structure (iv)



[0207] Of the carbons attached with marks C and G, a peak of the carbon C' and a peak of the carbon C'' appear in the second region, and a peak of the carbon G and a peak of the carbon G' appear in the third region.

[0208] Of the peaks which appear in the first to third regions as described above, peaks which are not based on the 3 propylene units-chain consisting of head-to-tail bonds are peaks based on the PPE-methyl group, the EPE-methyl group, the carbon C', the carbon C'', the carbon G and the carbon G'.

[0209] The peak area based on the PPE-methyl group can be evaluated by the peak area of the PPE-methine group (resonance in the vicinity of 30.6 ppm), and the peak area based on the EPE-methyl group can be evaluated by the peak area of the EPE-methine group (resonance in the vicinity of 32.9 ppm). The peak area based on the carbon C' can be evaluated by twice as much as the peak area of the methine carbon (resonance in the vicinity of 33.6 ppm) to which the methyl group of the carbon G is directly bonded; and the peak area based on the carbon C'' can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.2 ppm) of the methyl group of the carbon G'. The peak area based on the carbon G can be evaluated by the peak area of the adjacent methine carbon (resonance in the vicinity of 33.6 ppm); and the peak area based on the carbon G' can be also evaluated by the adjacent methine carbon (resonance in the vicinity of 33.2 ppm).

[0210] Accordingly, by subtracting these peak areas from the total peak areas of the second region and the third region, the peak areas based on the 3 propylene units-chains (PPP(mr) and PPP(rr)) consisting of head-to-tail bonds can be obtained.

[0211] Thus, the peak areas of PPP(mm), PPP(mr) and PPP(rr) can be evaluated, and hence the triad tacticity of the propylene unit chain consisting of head-to tail bonds can be determined.

[0212] In the propylene elastomer, the proportion of the inversely inserted units based on the 2,1-insertion in all propylene insertions, as measured by ¹³C-NMR, is not less than 0.5 %, preferably 0.5 to 2.0 %, more preferably 0.5 to 1.5 %. Further, the proportion of the inversely inserted units based on the 1,3-insertion is not more than 0.05 %, preferably 0.05 to 0.1 %.

preferably not more than 0.03 %.

[0213] The proportion of the 2,1-insertions to all of the propylene insertions in the propylene elastomer was calculated by the following formula with reference to "Polymer", 30 (1989) 1350.

Proportion of inversely inserted unit based on 2,1-insertion (%)

$$= \frac{0.25 I_{\alpha\beta}(\text{structure (iii)}) + 0.5 I_{\alpha\beta}(\text{structure (iv)})}{I_{\alpha\alpha} + I_{\alpha\beta}(\text{structure (iv)}) + 0.5 \{I_{\alpha\gamma} + I_{\alpha\beta}(\text{structure (iii)}) + I_{\alpha\delta}\}} \times 100$$

[0214] Naming of the peaks in the above formula was made in accordance with the method of Carman, et al. (Rubber Chem. Technol., 44 (1971), 781). $I_{\alpha\delta}$ denotes a peak area of the $\alpha\delta$ peak.

[0215] If it is difficult to determine the peak area of, for example, $I_{\alpha\delta}$ directly from the spectrum because of overlapping of the peaks, a carbon peak having a corresponding area can be substituted therefor.

[0216] The proportion (%) of the amount of the three propylene units-chains based on the 1,3-insertion was determined by dividing 1/2 as much as the area of the $\beta\gamma$ peak (resonance in the vicinity of 27.4 ppm) by the sum of all the methyl group peaks and 1/2 as much as the $\beta\gamma$ peak, and then multiplying the resulting value by 100.

[0217] The propylene elastomer has an intrinsic viscosity $[\eta]$, as measured in decahydronaphthalene at 135 °C, of 0.1 to 12 dl/g, preferably 0.5 to 12 dl/g, more preferably 1 to 12 dl/g.

[0218] The propylene elastomer is prepared by copolymerizing propylene and ethylene in the presence of the aforesaid olefin polymerization catalysts. The copolymerization can be carried out by a liquid phase polymerization (e.g., a suspension polymerization or a solution polymerization) or a gas phase polymerization.

[0219] In the liquid phase polymerization, the same inert hydrocarbon solvent as used for preparing the aforesaid catalyst can be used, and propylene and/or ethylene can be also used as a solvent.

[0220] In the suspension polymerization, the temperature for copolymerizing propylene and ethylene is usually -50 to 100 °C, preferably 0 to 90 °C. In the solution polymerization, the temperature is usually 0 to 250 °C, preferably 20 to 200 °C. In the gas phase polymerization, the temperature is usually 0 to 120 °C, preferably 20 to 100 °C. The copolymerization pressure is usually atmospheric pressure to 100 kg/cm², preferably atmospheric pressure to 50 kg/cm². The copolymerization reaction can be carried out either batchwise, semicontinuously or continuously. Further, the copolymerization can be carried out in two or more stages having different reaction conditions.

[0221] The molecular weight of the resultant propylene elastomer can be regulated by allowing hydrogen to exist in the copolymerization system or by varying the copolymerization temperature and the copolymerization pressure.

[0222] The novel transition metal compound according to the invention can be used as an olefin polymerization catalyst component.

[0223] The olefin polymerization catalyst of the invention has a high polymerization activity and polyolefins prepared by the use of the catalyst have a narrow molecular weight distribution and a narrow composition distribution. When an α -olefin of 3 or more carbon atoms is used, a polymer having a lower melting point is obtainable as compared with a polymer obtained by using a conventional metallocene catalyst even though the polymers have the almost the same molecular weight.

[0224] By the use of the catalyst of the invention, a copolymer having a low melting point can be obtained even if the amount of recurring units derived from a comonomer is small. Further, because of the small amount of solvent-soluble components, the resultant copolymer has excellent properties such as transparency, heat-sealing and anti-blocking. Moreover, the synthesis of polypropylene can be made with fewer reaction steps and is more economic, as compared with the synthesis using a conventional metallocene catalyst when polypropylene having almost the same molecular weight is produced.

[0225] When a copolymer elastomer mainly containing ethylene units and propylene units is prepared using the olefin polymerization catalyst of the invention, the resultant elastomer has a high molecular weight. Such a copolymer elastomer has a high strength, and hence when used as a modifier the elastomer exhibits excellent effects in the improvement of impact strength and hardness of polyolefins. When the copolymer elastomer is used to prepare a propylene block copolymer, the resultant copolymer is well-balanced between heat resistance, rigidity or transparency and impact strength because the molecular weight of the copolymer elastomer can be increased. Also in the preparation of polyethylene, the resultant polyethylene has excellent mechanical strength such as impact strength, tensile strength and flexural strength for the same reason.

[0226] The propylene polymer which can be prepared has excellent rigidity, heat resistance, surface hardness, glossiness, transparency and impact resistance. Hence, it can be suitably used for, for example, various industrial parts, containers, films, nonwoven fabrics, or stretched yarns.

[0227] The propylene copolymer which can be produced has excellent transparency, rigidity, surface hardness, heat resistance, heat-sealing properties, anti-blocking properties, bleed resistance and impact resistance. Hence, it can be suitably used for, for example, films, sheets, containers, stretched yarns or nonwoven fabrics.

[0228] The propylene elastomer which can be produced has excellent heat resistance, impact absorbing properties, transparency, heat-sealing properties and anti-blocking properties. Hence, it can be singly used for, for example, films or sheets, and moreover can be suitably used as a modifier of a thermoplastic resin.

5 EXAMPLES

[0229] The present invention is described in more detail in the following Examples.

[0230] The intrinsic viscosity $[\eta]$, molecular weight distribution (Mw/Mn), stereoregularity (mmmm), proportion of inversely inserted units, melting point (Tm), melt flow rate (MFR), flexural modulus (FR), heat distortion temperature (HDT), heat seal-starting temperature and heat seal-starting temperature after heat treatment, izod impact strength (IZ) and film impact strength are measured by the following methods.

Intrinsic viscosity $[\eta]$

[0231] The intrinsic viscosity $[\eta]$ was measured in decahydronaphthalene at 135 °C, and expressed as dl/g.

Molecular weight distribution (Mw/Mn)

[0232] The molecular weight distribution (Mw/Mn) was measured in the following manner using GPC-150C produced by Millipore Co.

[0233] A separation column of TSK-GNH-HT having a diameter of 72 mm and a length of 600 mm was used, and the column temperature was set to 140 °C. A sample (concentration 0.1 % by weight, amount: 500 microliters) was moved in the column at a rate of 1.0 ml/min using o-dichlorobenzene (available from Wako Junyaku Kogyo K.K.) as a mobile phase and 0.025 % by weight of BHT (Takeda Chemical Industries, Ltd.) as an antioxidant. A differential refractometer was used as a detector. Standard polystyrenes available from Toso Co., Ltd. were used for $M_w < 1,000$ and $M_w > 4 \times 10^6$, and polystyrenes available from Pressure Chemical Co. were used for $1,000 < M_w < 4 \times 10^6$.

Stereoregularity (mm triad tacticity and mmmm pentad tacticity)

[0234] mm triad tacticity was measured as mentioned above.

[0235] mmmm pentad tacticity was measured as follows.

[0236] About 50 mg of a sample was completely dissolved in a mixed solvent containing 0.5 ml of o-dichlorobenzene (or hexachlorobutadiene) and 0.1 ml of deuterated benzene in a NMR sample tube (diameter: 5 mm) at about 120 °C, and then the ^{13}C -NMR spectrum was measured (nuclear species: ^{13}C , mode: perfect proton decoupling, temperature: 120 °C) by a GX500 type NMR measuring apparatus produced by Japan Electron Optics Laboratory Co., Ltd.

[0237] On the ^{13}C -NMR spectrum, an area of a peak having resonance in the lowest magnetic field (21.8 ppm according to A. Zambelli, P. Locatelli, G. Bajo and F.A. Bovey, "Macromolecules", 8, 687 (1975)) was divided by a total area of all peaks of the methyl groups, and the resultant value was taken as a mmmm pentad tacticity value.

40 Proportion of inversely inserted units

[0238] For each of the polymers obtained in Examples 3 and 4 and Comparative Example 1, the proportions of the inversely inserted units based on the 2,1-insertion and the 1,3-insertion of a propylene monomer present in the propylene chain of the polymer were determined from the ^{13}C -NMR spectrum and the following formulae.

$$2,1\text{-insertion (\%)} = \frac{0.5 \text{I}\alpha\beta}{\text{I}\alpha\alpha + \text{I}\alpha\beta} \times 100$$

$$1,3\text{-insertion (\%)} = \frac{0.5 \text{I}\alpha\beta}{\text{I}\alpha\alpha + \text{I}\alpha\beta + \text{I}\alpha\delta} \times 100$$

wherein $\text{I}\alpha\alpha$ is the total area of the $\alpha\alpha$ carbon peaks (resonances in the vicinity of 42.0 ppm and 46.2 ppm), $\text{I}\alpha\beta$ is the total area of the $\alpha\beta$ carbon peaks (resonances in the vicinity of 30.2 ppm and 35.6 ppm), and $\text{I}\alpha\delta$ is the area of the $\alpha\delta$ carbon peak (resonance in the vicinity of 37.1 ppm). Naming of the peaks (e.g., $\alpha\alpha$) was made in accordance with the classification by Carman, et al. (C.J. Carman and C.E. Wilkes, Rubber Chem. Technol., 44, 781 (1971)).

[0239] The proportions of the inversely inserted units in other Examples were measured by the method described before.

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Melting point (T_m)

[0240] The melting point was determined from an endothermic curve given by heating about 5 mg of a sample charged in an aluminium pan to 200 °C at a rate of 10 °C/min, keeping it at 200 °C for 5 minutes, then cooling it to room temperature at a rate of 20 °C/min and heating it again at a rate of 10 °C/min. The measurement was conducted using a DSC-7 type apparatus produced by Perkin Elmer Co.

Melt flow rate (MFR)

[0241] The MFR is measured in accordance with ASTM D 1238 under a load of 2.16 kg at 230 °C.

Flexural modulus (FM)

[0242] The FM is measured in accordance with ASTM D 790 using a specimen of 12.7 mm (width) X 6.4 mm (thickness) X 127 mm (length) prepared by injection molding at a resin temperature of 200 °C and a molding temperature of 40 °C at a distance between spurs of 100 mm and a rate of flexing of 2 mm/min.

Heat distortion temperature (HDT)

[0243] The HDT is measured in accordance with ASTM D 648 under a load of 4.6 kg/cm².

Heat seal-starting temperature and heat seal-starting temperature after heat treatment

[0244] Using a T-die film having a width of 30 cm and a thickness of 50 µm prepared using a single screw extruder having a diameter of 30 mm under the conditions of a resin temperature of 210 °C (at a portion of die of extruder), a take-off speed of 3 m/min and a temperature of cooling roll of 25 °C, heat sealing of two films is carried out using a heat sealer by sealing at various seal temperatures under the conditions of a heat seal pressure of 2 kg/cm², a seal time of 1 second and a width of 5 mm, to prepare a sealed film. The above-prepared sealed film was allowed to cool.

[0245] The heat seal-starting temperature is defined as the temperature of the heat sealer when the peeling resistance of the sealed film becomes 300 g/25 mm, under such conditions that the sealed film is peeled off at 23 °C, a peeling speed of 200 mm/min and a peeling angle of 180 °.

[0246] Separately, another sealed film was subjected to heat treatment at 50 °C for 7 days. The heat seal-starting temperature after heat treatment was measured using the heat treated specimen.

Izod impact strength (IZ)

[0247] The IZ is measured in accordance with ASTM D 256 at 23 °C using a notched specimen of 12.7 mm (width) x 6.4 mm (thickness) X 64 mm (length).

[0248] The specimen is prepared by injection molding at a resin temperature of 200 °C and a molding temperature of 40 °C using a polypropylene composition obtained by dry-blending 20 % by weight of a polymer according to the present invention and 80 % by weight of a polypropylene (HIPOL™, grade J 700, melt flow rate: 11 g/10 min (at 230 °C), density: 0.91, manufactured by Mitsui petrochemical Industries, Ltd.), and melt-kneading at 200 °C using a twin-screw extruder.

Film impact strength

[0249] The film impact strength is measured using a film impact tester (manufactured by Toyo Seiki K.K., diameter of impact head bulb: 1/2 inch (12.7 mm φ)).

Example 1

Synthesis of rac-dimethylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride

Synthesis of 4-isopropyl-2,7-dimethylindene (compound 1)

[0250] A 1-liter reactor thoroughly purged with nitrogen was charged with 90 g (0.67 mol) of aluminium chloride and 150 ml of carbon disulfide, and to the reactor was dropwise added a solution of 47 ml (0.30 mol) of p-cymene and 33 ml (0.3 mol) of methacryloyl chloride in 30 ml of carbon disulfide at a temperature of 20 to 25 °C. The mixture was

reacted at room temperature for 12 hours and then added to 1 kg of ice, followed by extraction with ether. The obtained ether solution was washed with a saturated aqueous solution of sodium hydrogencarbonate and then water, and concentrated to obtain 68 g of an oil. This oil was purified by silica gel column chromatography (eluting solution: n-hexane) to obtain 42 g of a mixture (mixture 1) of 2,4-dimethyl-7-propyl-1-indanone and 2,7-dimethyl-4-isopropyl-1-indanone (yield: 67 %).

[0251] A 1-liter reactor thoroughly purged with nitrogen was charged with 2.82 g (0.075 mol) of lithium aluminium hydride and 200 ml of ether, and to the reactor was dropwise added a mixture of 36.5 g (0.18 mol) of the mixture 1 and 150 ml of ether while cooling with ice. After the dropwise addition was completed, the mixture was stirred at room temperature for 30 minutes and then refluxed for 1 hour. After the reaction was completed, the reaction mixture was worked up by a conventional procedure and then extracted with ether. The obtained ether solution was washed with a saturated aqueous solution of sodium hydrogencarbonate and water, and dried over sodium sulfate. The ether layer was concentrated to obtain 36 g of a solid. This solid was slurried in 100 ml of n-hexane and the solvent was evaporated off to obtain 30 g of a mixture (mixture No.2) of 2,4-dimethyl-7-isopropyl-1-indanol and 2,7-dimethyl-4-isopropyl-1-indanol (yield: 82 %).

[0252] A 1-liter reactor thoroughly purged with nitrogen was charged with 25 g (0.12 mol) of the mixture 2 and 500 ml of benzene. To the reactor was added 50 mg (0.55 mmol) of paratoluene sulfonic acid monohydrate, and the mixture was refluxed for 1 hour. After the reaction was completed, the reaction mixture was poured into 30 ml of saturated sodium hydrogencarbonate solution. The resulting organic layer was washed with water and then dried over anhydrous sodium sulfate. The organic layer was concentrated to give an oil which was then distilled to obtain 20 g of the title compound 1 (yield: 90 %).

[0253] The NMR data of the title compound 1 is shown in Table 1.

Synthesis of 1,1'-dimethylsilyl-bis(4-isopropyl-2,7-dimethylindene) (compound 2)

[0254] A 200-ml reactor thoroughly purged with nitrogen was charged with 9.5 g (51 mmol) of the title compound 1, 7.7 ml (51 mmol) of tetramethylethylenediamine and 60 ml of diethyl ether, followed by cooling to -10 °C. To the solution was added a solution of n-butyllithium (51 mmol) in hexane. After heating to room temperature, the solution was cooled again to -10 °C, 3.1 ml (25.5 mmol) of dimethyldichlorosilane was dropwise added over 30 minutes and the reaction was carried out for 1 hour. After the reaction was completed, the reaction solution was added to 40 ml of a saturated aqueous solution of ammonium chloride, then extracted with n-hexane, washed with water and dried over magnesium sulfate. The salt was removed, and the resulting organic layer was concentrated under reduced pressure to obtain a yellow oil which was purified by silica gel column chromatography (eluting solution: n-hexane) to obtain 5.4 g of the title compound 2 as a colorless amorphous product (yield: 50 %).

[0255] The NMR data of the title compound 2 is shown in Table 1.

Synthesis of rac-dimethylsilyl-bis(1-(4-isopropyl-2,7-dimethylindenyl))zirconium dichloride (compound 3)

[0256] A 300-ml reactor thoroughly purged with nitrogen was charged with 5.4 g (12.6 mmol) of the title compound 2 and 100 ml of tetrahydrofuran, and the content in the reactor was cooled to -78 °C and stirred. To the reactor was dropwise added 16 ml of n-butyllithium (a solution in n-hexane, 1.58 N, 25.2 mmol) over 20 minutes, and the mixture was stirred for another 1 hour keeping the temperature to prepare an anion solution which was then slowly heated to room temperature.

[0257] Separately, 100 ml of tetrahydrofuran was charged in a 300-ml reactor thoroughly purged with nitrogen, cooled to -78 °C and stirred. To the reactor was slowly added 2.94 g (12.6 mmol) of zirconium tetrachloride, followed by heating to room temperature. To the mixture was dropwise added the anion solution prepared above over 30 minutes, followed by stirring at room temperature for 12 hours. After the reaction was completed, the reaction mixture was concentrated under reduced pressure and a solid precipitate was washed three times with 300 ml of hexane to remove insoluble substances. The obtained hexane solution was concentrated to about 50 ml, and the solution was cooled at 6 °C for 12 hours. ¹H-NMR analysis of the solid obtained, 1.78 g (yield: 24 %), showed that it was a mixture of a racemic modification and a mesoisomer (4 : 1). This mixture was recrystallized from 100 ml of hexane to obtain 0.22 g of the title compound 3 as a yellow prismatic crystal (yield: 3 %). The result of the FD mass spectrometry of the title compound 3 was 588 (M⁺).

[0258] The NMR data of the title compound 3 is shown in Table 1.

Example 2

Synthesis of rac-diphenylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride

Synthesis of 1,1'-diphenylsilyl-bis(4-isopropyl-2,7-dimethylindene) (compound 4)

[0259] The procedure of the synthesis of the title compound 2 in Example 1 was repeated except that 120 mg of copper cyanide was used in place of tetramethylethylenediamine and 5.7 ml of diphenyldichlorosilane in place of dimethyldichlorosilane.

[0260] The title compound 4 was obtained as a colorless amorphous product in an amount of 7.2 g (yield: 49 %).

[0261] The NMR data of the title compound 4 is shown in Table 1.

Synthesis of rac-diphenylsilyl-bis{1-(4-isopropyl-2,7-dimethylindenyl)}zirconium dichloride (compound 5)

[0262] The procedure of the synthesis of the title compound 3 in Example 1 was repeated except that 7.1 g (12.9 mmol) of the title compound 4 was used in place of the title compound 2 and 3.01 of zirconium tetrachloride in place of 2.94 g.

[0263] The title compound 5 was obtained as an yellow prismatic crystal in an amount of 1.10 g (yield: 12 %). The result of the FD mass spectrometry of the compound 5 was 712 (M⁺).

[0264] The NMR data of the title compound 5 is shown in Table 1.

Table 1

NMR Data	
Compound No.	¹ H-NMR Spectrum (CDCl ₃ , ppm)
1	1.26(6H, d, J=7.2Hz), 2.70(3H, s), 2.38(3H, s), 2.88(1H, q, J=7.0Hz), 3.27(2H, s), 6.54(1H, s), 6.90(1H, s), 7.10(1H, s)
2	1.60(12H, d, J=7.2Hz), 0.94~1.14(6H, m), 1.91~2.06(6H, m), 2.26(6H, s), 2.71(2H, q, J=7.2Hz), 3.49(2H, s), 6.49(2H, s), 6.74(2H, s), 7.06(2H, s)
3	1.20(12H, d, J=7.2Hz), 1.29(6H, s), 2.21(6H, s), 2.33(6H, s), 2.81(2H, q, J=7.0Hz), 6.70(2H, s), 7.01(2H, s), 7.26(2H, s)
4	1.06(6H, d, J=7.2Hz), 1.26(6H, d, J=7.2Hz), 1.80(3H, s), 2.10(6H, s), 2.24(3H, s), 2.80(2H, s), 4.36(4H, br.s), 6.16(2H, s), 6.60-7.68(14H, m)
5	0.92(12H, d, J=6.8Hz), 2.02(6H, s), 2.36(6H, s), 2.60(2H, q, J=6.8Hz), 6.80(2H, s), 6.90(2H, s), 6.99(2H, s), 7.45-7.50(6H, m), 8.12-8.16(4H, m)

Example 3

[0265] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triisobutylaluminium, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropyl-1-indenyl)}zirconium dichloride to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0266] The amount of the polymer obtained was 158 g and the polymerization activity was 158 kg-PP/mmol-Zr. The polymer had an [η] of 4.55 dl/g, a Mw/Mn of 2.2, an mmmm pentad value of 95.5 %, a proportion of the 2,1-insertion of 0.90 % and a Tm of 147 °C.

Example 4

[0267] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triethylaluminium, 0.001 mmol (in terms of Zr atoms) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride and 0.002 mmol (in terms of B atoms) of tris(pentafluorophenyl)boron to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0268] The amount of the polymer obtained was 94 g and the polymerization activity was 94 kg-PP/mmol-Zr. The

polymer had an $[\eta]$ of 4.75 dl/g, a Mw/Mn of 2.3, an mmmm pentad value of 96.4 %, a proportion of the 2,1-insertion of 0.80 % and a Tm of 148 °C.

Comparative Example 1

[0269] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene, followed by warming to 40 °C. To the autoclave were added 0.2 mmol of triisobutylaluminium, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2-methyl-4-isopropylindenyl)}zirconium dichloride to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours.

[0270] The amount of the polymer obtained was 125 g and the polymerization activity was 125 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 3.47 dl/g, a Mw/Mn of 2.1, an mmmm pentad value of 96.2 %, a proportion of the 2,1-insertion of 0.40 % and a Tm of 152 °C.

Example 5

[0271] A 1-liter glass reactor thoroughly purged with nitrogen was charged with 500 ml of toluene, and propylene was fed at a rate of 100 liters/hr, followed by warming to 50 °C. To the reactor was added a solution obtained by precontacting 3.5 mmol of methylaluminoxane and 0.01 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride in toluene, to polymerize propylene at 50 °C for 20 minutes. After the polymerization, the solution was poured into a methanol-hydrochloric acid solution, and the resulting mixture was filtered to give a polymer which was dried at 80 °C for 10 hours.

[0272] The amount of the polymer obtained was 32.6 g and the polymerization activity was 8.2 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 1.37 dl/g, a Mw/Mn of 2.2 and a Tm of 148 °C.

Comparative Example 2

[0273] The procedures of Example 5 were repeated except that rac-ethylenebis{1-(2, 4, 7-trimethylindenyl)}zirconium dichloride was used in place of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride.

[0274] The amount of the polymer obtained was 23.1 g and the polymerization activity was 5.8 kg-PP/mmol-Zr. The polymer had an $[\eta]$ of 0.44 dl/g, a Mw/Mn of 2.3 and a Tm of 150 °C. This polymer had a molecular weight which was much lower than that of the polymer obtained in Example 5.

Example 6

Preparation of solid catalyst component (a)

[0275] A 500-ml reactor thoroughly purged with nitrogen was charged with 25 g of silica (F-948, available from Fuji Devison Co.) which had been dried at 200 °C for 6 hours in a stream of nitrogen and 310 ml of toluene, and the system was set to 0 °C with stirring. To the system was dropwise added 90 ml of an organoaluminium oxy-compound (methylaluminoxane available from Schering Co., diluted in toluene, 2.1 mol/liter) over 60 minutes in a nitrogen atmosphere. Then, the mixture was reacted at the same temperature for 30 minutes and further at 90 °C for 4 hours. The reaction system was allowed to cool and when the temperature reached 60 °C, the supernatant was decanted off and the residue was washed three times with 150 ml of toluene at room temperature to obtain a solid catalyst component (a) containing 6.8 mmol of Al per 1 g of silica.

Preparation of solid catalyst component (b)

[0276] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.9 mmol of triisobutylaluminium were successively added to the reactor and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to prepolymerize propylene. The supernatant was decanted off and then the residue washed three times with 150 ml of toluene to obtain a solid catalyst component (b) in which Zr and Al were supported in amounts of 0.011 mmol and 4.48 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0277] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 3.6 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atom) of the solid catalyst component (b), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0278] The amount of the polymer (powder) obtained was 75 g, the amount (SP) of the polymer dissolved in the solvent was 1.9 g (2.5 % by weight), and the polymerization activity was 38.5 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 6.0 dg/min, a Mw/Mn of 2.6, an ethylene content of 2.9 % by mol and a Tm of 126 °C.

Example 7Preparation of solid catalyst component (c)

[0279] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.9 mmol of triisobutylaluminium were successively added to the reactor, and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to polymerize propylene. The supernatant was decanted off, and then the residue was washed three times with 150 ml of toluene to obtain a solid catalyst component (c) in which Zr and Al were supported in amounts of 0.011 mmol and 4.55 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0280] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 3.6 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atom) of the solid catalyst component (c), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0281] The amount of the polymer (powder) obtained was 59 g, the amount (SP) of the polymer dissolved in the solvent was 2.5 g (4.0 % by weight), and the polymerization activity was 30.7 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 5.8 dg/min, a Mw/Mn of 2.6, an ethylene content of 2.9 % by mol and a Tm of 127 °C.

Comparative Example 3Preparation of solid catalyst component (d)

[0282] A 200-ml reactor thoroughly purged with nitrogen was charged with 50 ml of n-hexane, and to the reactor were added 10.5 mmol (in terms of Al atoms) of the solid catalyst component (a) obtained above and 0.03 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis{1-(2-methyl-4-isopropylindenyl)}zirconium dichloride, followed by stirring for 20 minutes. Then, 100 ml of n-hexane and 0.09 mmol of triisobutylaluminium were successively added to the reactor, and the mixture was stirred for 10 minutes. Thereafter, propylene gas (2.2 liters/hr) was passed through the reactor at 20 °C for 4 hours to prepolymerize propylene. The supernatant was decanted off, and then the residue was washed three times with 150 ml of toluene to obtain a solid catalyst component (d) in which Zr and Al were supported in amounts of 0.011 mmol and 4.35 mmol, respectively, per 1 g of the solid catalyst.

Polymerization

[0283] 750 ml of purified n-hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 5.2 % by mol). To the reaction system were added 1.0 mmol of triisobutylaluminium and 0.002 mmol (in terms of Zr atoms) of the solid catalyst component (d), and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour at a total pressure of 2 kg/cm²-G. After the polymerization, the reaction mixture was filtered to remove the solvent, the resulting polymer was washed with hexane and dried at 80 °C for 10 hours.

[0284] The amount of polymer (powder) obtained was 67 g, and a small amount of the polymer adhered to the autoclave wall was observed. The amount (SP) of the polymer dissolved in the solvent was 9.0 g (12.0 % by weight). The polymerization activity was 38 kg-copolymer/mmol-Zr. The polymer powder had an MFR of 12 dg/min, a Mw/Mn of 2.5, an ethylene content of 5.0 % by mol and a Tm of 127 °C.

[0285] When the above polymerization procedure is performed in an industrial scale, it is presumed that the polymer which adheres to the autoclave wall will cause a reduced heat transfer efficiency, and that the high SP value will cause not only a reduced polymer yield but also an increased viscosity of the solvent removed, resulting in difficult operation.

Example 8

[0286] A 2-liter autoclave thoroughly purged with nitrogen was charged with 500 g of propylene. The temperature of the autoclave was elevated to 40 °C, and to the autoclave were added 0.2 mmol of triisobutylaluminum, 0.2 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis(1-(2,7-dimethyl-4-isopropylindenyl)) zirconium dichloride, to polymerize propylene at 50 °C for 1 hour. After the polymerization, the autoclave was released to remove propylene, and the resulting polymer was dried at 80 °C for 10 hours under a reduced pressure.

[0287] The amount of the propylene polymer obtained was 158 g, and the polymerization activity was 158 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity $[\eta]$ of 4.55 dl/g. In the propylene polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.4 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.87 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.03 %.

[0288] The polymer had a melt flow rate (MFR) of 12.5 g/10 min, a flexural modulus (FM) of 12500 kg/cm², and a heat distortion temperature of 105 °C.

Example 9

[0289] 750 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen and stirred at 25 °C for 20 minutes in a propylene/ethylene mixed gas atmosphere (ethylene: 2.9 % by mol). To the reaction system were added 0.25 mmol of triisobutylaluminum, 0.5 mmol of methylaluminoxane and 0.0015 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis(1-(2,7-dimethyl-4-isopropylindenyl))zirconium dichloride, and the temperature of the system was elevated to 50 °C to polymerize the monomers for 1 hour while keeping the total pressure at 2 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 80 °C for 10 hours under a reduced pressure.

[0290] The amount of the propylene copolymer obtained was 26.9 g, and the polymerization activity was 17.9 kg-polymer/mmol-Zr. The copolymer had an intrinsic viscosity $[\eta]$ of 2.2 dl/g and an ethylene content of 3.0 % by mol. In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 97.3 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.9 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was 0.04 %.

[0291] The film of the copolymer had a heat seal-starting temperature of 118 °C and a heat seal-starting temperature after heat treatment of 120 °C.

[0292] The results are shown in Table 2.

Example 10

[0293] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and 1 mmol of triisobutylaluminum was added thereto. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a pressure of 1.5 kg/cm², and propylene was then fed to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.3 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atoms) of rac-dimethylsilyl-bis(1-(2,7-dimethyl-4-isopropylindenyl))zirconium dichloride to polymerize the monomers for 20 minutes while propylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 110 °C for 10 hours under a reduced pressure.

[0294] The amount of the propylene copolymer obtained was 21.2 g, and the polymerization activity was 21 kg-polymer/mmol-Zr. The copolymer had an intrinsic viscosity $[\eta]$ of 1.5 dl/g and an ethylene content of 4.7 % by mol. In the propylene copolymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 96.9 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 1.1 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.04 %.

[0295] The film of the copolymer had a heat seal-starting temperature of 107 °C and a heat seal-starting temperature

after heat treatment of 111 °C.

[0296] The results are shown in Table 2.

Example 11

[0297] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen. Then, to the autoclave was added 1 mmol of triisobutylaluminum and was fed 60 liters of propylene gas. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.45 mmol of methylaluminoxane and 0.0015 mmol (in terms of Zr atom) of rac-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride to polymerize the monomers for 40 minutes while ethylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol, and dried at 110 °C for 10 hours under reduced pressure.

[0298] The amount of the polymer obtained was 47.2 g. The polymerization activity was 31.5 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity [η] of 2.0 dl/g and an ethylene content of 27.0 % by mol. In the polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.4 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.88 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.05 %.

[0299] The film of the copolymer had a film impact strength of 6000 kgf-cm/cm, and the composition with polypropylene had IZ of 35 kg-cm/cm and a melt flow rate (MFR) of 9.3 g/10 min.

[0300] The results are shown in Table 2.

Example 12

[0301] 900 ml of hexane was introduced into a 2-liter autoclave thoroughly purged with nitrogen, and 1 mmol of triisobutylaluminum was added thereto. After elevating the temperature of the reaction system to 70 °C, ethylene was fed to the system to a pressure of 2.0 kg/cm², and then propylene was fed to the system to a total pressure of 8 kg/cm²-G. Then, to the reaction system were added 0.3 mmol of methylaluminoxane and 0.001 mmol (in terms of Zr atom) of rac-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride, to polymerize the monomers for 10 minutes while propylene was continuously fed to keep the total pressure at 8 kg/cm²-G. After the polymerization, the autoclave was released, the resulting polymer was recovered in a large amount of methanol and dried at 110 °C for 10 hours under reduced pressure.

[0302] The amount of the polymer obtained was 16.8 g and the polymerization activity was 16.8 kg-polymer/mmol-Zr. The polymer had an intrinsic viscosity [η] of 1.7 dl/g and an ethylene content of 8.5 % by mol. In the polymer, the triad tacticity of the propylene unit chain consisting of head-to-tail bonds was 95.6 %, the proportion of the inversely inserted units based on the 2,1-insertion of the propylene monomer was 0.62 %, and the proportion of the inversely inserted units based on the 1,3-insertion of the propylene monomer was not more than 0.05 %.

[0303] The film of the copolymer had a heat seal-starting temperature of 90 °C and a heat seal-starting temperature after heat treatment of 93 °C.

[0304] The results are shown in Table 2.

Table 2

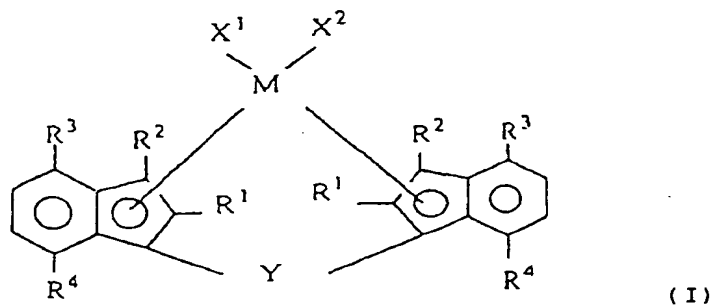
Example	Intrinsic viscosity $[\eta]$	Melt- ing point (°C)	Ethylene content (mol %)	Heat seal- starting tempera- ture (°C)	Heat seal- starting tempera- ture after heat treatment	Film impact strength (kg·cm /cm)
Ex. 9	2.2	120	3	118	120	-
Ex. 10	1.5	110	4.7	107	111	-
Ex. 11	2	-	27	-	-	6000
Ex. 12	1.7	90	8.5	90	93	-

Table 2 (Continued)

Example	IZ of composition with polypropylene (kgf·cm/cm)	MFR of composition with polypropylene (g/10 min)
Ex. 9	-	-
Ex. 10	-	-
Ex. 11	35	9.3
Ex. 12	-	-

Claims

1. A transition metal compound of formula (I):



wherein

M is zirconium;

R¹ and R², which may all be identical or different from each other, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms;

R³ is an isopropyl group;

R⁴ is a methyl group;

X¹ and X², which may be identical or different, are each a hydrogen atom, a halogen atom or a hydrocarbon group of 1 to 20 carbon atoms; and

Y is a divalent silicon-containing group selected from an alkylsilylene group, an alkylarylsilylene group and an arylsilylene group.

2. An olefin polymerization catalyst comprising:

(A) a transition metal compound of formula (I) as defined in claim 1; and

(B) at least one compound selected from:

(B-1) an organoaluminium oxy-compound, and

(B-2) a compound which reacts with the transition metal compound of formula (I) to form an ion pair.

3. An olefin polymerization catalyst according to claim 2 which further comprises

(C) an organoaluminium compound.

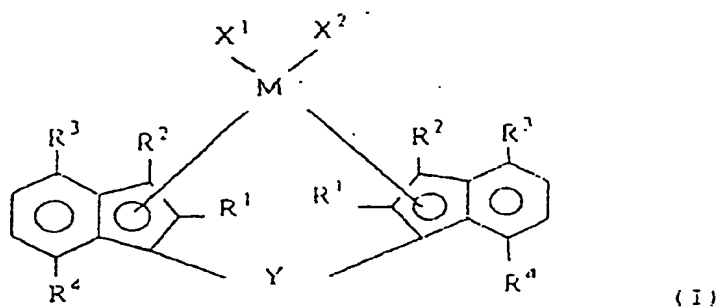
4. An olefin polymerization catalyst according to claim 2 or 3 which further comprises a fine particle carrier, components (A) and (B) being supported on said carrier.

5. An olefin polymerization catalyst according to claim 2 or 3 which further comprises a fine particle carrier and a prepolymerized olefin polymer produced by prepolymerization.

6. A process for olefin polymerization comprising polymerizing or copolymerizing an olefin in the presence of an olefin polymerization catalyst as defined in any one of claims 2 to 5.

Patentansprüche

1. Übergangsmetallverbindung der Formel (I):



worin M Zirkonium ist;

R¹ und R², die alle identisch oder voneinander verschieden sein können, jeweils ein Wasserstoffatom, ein Halogenatom oder eine Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen sind;

R³ eine Isopropylgruppe ist;

R⁴ eine Methylgruppe ist;

X¹ und X², die alle identisch oder voneinander verschieden sein können, jeweils ein Wasserstoffatom, ein Halogenatom oder eine Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen sind; und

Y eine zweiwertige Silicium enthaltende Gruppe ist, gewählt aus einer Alkylsilylengruppe, einer Alkylarylsilylengruppe und einer Arylsilylengruppe.

2. Olefin-Polymerisationskatalysator, umfassend:

(A) eine Übergangsmetallverbindung der Formel (I), wie in Anspruch 1 definiert; und

(B) mindestens eine Verbindung, gewählt aus:

(B-1) einer Organoaluminiumoxyverbindung und

(B-2) einer Verbindung, die mit der Übergangsmetallverbindung der Formel (I) reagiert unter Bildung eines Ionenpaares.

3. Olefin-Polymerisationskatalysator gemäß Anspruch 2, weiterhin umfassend:

(C) eine Organoaluminiumverbindung.

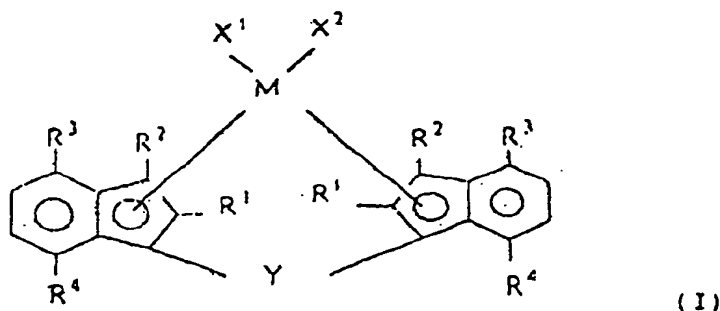
4. Olefin-Polymerisationskatalysator gemäß Anspruch 2 oder 3, weiterhin umfassend einen Feinteilchenträger, wobei die Komponenten (A) und (B) auf dem Träger getragen werden.

5. Olefin-Polymerisationskatalysator gemäß Anspruch 2 oder 3, weiterhin umfassend einen Feinteilchenträger und ein durch Prepolymerisation erzeugtes prepolymerisiertes Olefinpolymer.

6. Verfahren für die Olefin-Polymerisation, umfassend das Polymerisieren oder Copolymerisieren eines Olefins in Gegenwart eines Olefin-Polymerisationskatalysators, wie in mindestens einem der Ansprüche 2 bis 5 definiert.

Revendications

1. Dérivé de métal de transition de formule (I) :



dans laquelle M représente un atome de zirconium,

R¹ et R² qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné ayant 1 à 20 atomes de carbone,

R³ représente un groupe isopropyle,

R⁴ représente un groupe méthyle,

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X¹ et X² qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un atome d'halogène ou un groupe hydrocarboné ayant 1 à 20 atomes de carbone, et
Y représente un groupe divalent renfermant du silicium, choisi parmi les groupes alkylsilylène, les groupes alkylarylsilylène et les groupes arylsilylène.

5
2. Catalyseur de polymérisation des oléfines, qui comprend :

- (A) un dérivé de métal de transition de formule (I) tel que défini dans la revendication 1, et
(B) au moins un composé choisi parmi :

10
(B-1) les composés organoaluminium du type oxy, et
(B-2) les composés qui réagissent avec le dérivé de métal de transition de formule (I) pour former une paire d'ions.

15 3. Catalyseur de polymérisation des oléfines selon la revendication 2, qui renferme en outre

(C) un composé organoaluminium.

20 4. Catalyseur de polymérisation des oléfines selon la revendication 2 ou 3, qui comprend en outre un support en fines particules, les constituants (A) et (B) étant fixés sur ledit support.

5. Catalyseur de polymérisation des oléfines selon la revendication 2 ou 3, qui comprend en outre un support en fines particules et un polymère d'oléfine prépolymérisée, produit par prépolymérisation.

25 6. Procédé de polymérisation des oléfines, qui comprend la polymérisation ou la copolymérisation d'une oléfine en présence d'un catalyseur de polymérisation des oléfines, tel que défini dans l'une quelconque des revendications 2 à 5.